DEC 28 1916
UNIV. OF VICT.
LIBRARY

VOLUME VIII SECOND SERIES NUMBER 6

THE PHYSICAL REVIEW

A JOURNAL OF EXPERIMENTAL AND THEORETICAL PHYSICS

CONDUCTED BY

THE AMERICAN PHYSICAL SOCIETY

BOARD OF EDITORS

FREDERICK BEDELL, Managing Editor

H. A. BUMSTEAD J. S. AMES E. P. LEWIS
C. E. MENDENHALL E. BUCKINGHAM W. C. SABINE
A. G. WEBSTER A. A. MICHELSON A. TROWBRIDGE

DECEMBER, 1916

The Dielectric Constant of Aqueous Solutions. ELMER A. HARRINGTON 581
The Existence of a Subelectron? R. A. MILLIKAN 595
The Electrical Conductivity of a Bunsen Flame for Small Distances between the Electrodes. NORMAN HURD RICKER 626
On the Mobilities of Gas Ions in High Electric Fields. LEONARD B. LOEB 633
The Properties of Slow Canal Rays. A. J. DEMPSTER 651
A Direct Reading Precision Refractometer with Uniformly Divided Scale. G. W. MOFFITT 663
On a Modification of the Hilger Sector Photometer Method for Measuring Ultra-violet Absorption and its Application in the Case of Certain Derivatives of Fluoran. H. E. HOWE 674
The Distribution of Angular Velocities Among Diatomic Gas Molecules. EDWIN C. KEMBLE 689
On the Occurrence of Harmonics in the Infra-Red Absorption Spectra of Gases. EDWIN C. KEMBLE 701
On the Ionization of Gases by Alpha Rays. H. A. BUMSTEAD 715
The Magnetic Properties of Hematite. T. TOWNSEND SMITH 721
A Redetermination of the Absolute Value of the Coefficient of Viscosity of Air. ERTLE LESLIE HARRINGTON 738
New Books 752
Errata 753
Index 754

PUBLISHED BY
THE AMERICAN PHYSICAL SOCIETY
LANCASTER, PA., AND ITHACA, N. Y.
Entered at the post-office, at Lancaster, Pa., as second class matter

THE AMERICAN PHYSICAL SOCIETY

OFFICERS AND MEMBERS OF COUNCIL

President:	R. A. MILLIKAN	University of Chicago, Chicago, Ill.
Vice-President:	H. A. BUMSTEAD	Yale University, New Haven, Conn.
Secretary:	A. D. COLE	Ohio State University, Columbus, Ohio.
Treasurer:	J. S. AMES	Johns Hopkins University, Baltimore, Md.

The Council consists of the officers of the Society named above, all living Past Presidents and eight elected members as follows:

Past Presidents: A. A. Michelson, A. G. Webster, Carl Barus, E. L. Nichols, Henry Crew, W. F. Magie, Ernest Merritt.

Elected Members: H. T. Barnes, W. J. Humphreys, C. K. Burgess, D. C. Miller, C. E. Mendenhall, G. W. Stewart, Irving Langmuir, G. B. Pegram.

THE PHYSICAL REVIEW

Annual Subscription, throughout the Postal Union, $6.00
Single Copies, postpaid, $ .60

THE PHYSICAL REVIEW is conducted by a BOARD OF EDITORS, named on the outside cover

Subscriptions should be sent to THE PHYSICAL REVIEW, *41 North Queen Street, Lancaster, Pa.*, or *Ithaca, N. Y.*

Two volumes of THE PHYSICAL REVIEW are published annually, these volumes beginning in January and July, respectively, and containing six numbers each.

A limited number of complete sets of the REVIEW, both First and Second Series, will be supplied at the price of $3.00 per volume for all volumes, carriage extra. When they can be furnished without breaking a set, separate back volumes will be supplied at the same price, and single back numbers will be mailed to any address in the Postal Union at the price of $.60 per copy.

Back numbers will be furnished to members at a discount of ten per cent., provided a statement of membership accompanies the order. When a member's name has been dropped from the mailing list of the Review on account of non-payment of dues, his name will be restored to the mailing list when dues are paid; and any numbers that he has failed to receive in the interim will be furnished without cost upon application to the Review.

First Series. From July 1, 1893, to January 1, 1913, the REVIEW was conducted by Edward L. Nichols, Ernest Merritt and Frederick Bedell, with the financial support of Cornell University. During this period thirty-five volumes were issued, constituting the First Series. The first four volumes of the First Series were issued annually; subsequent volumes were issued semi-annually.

Second Series. On January first, 1913, the Review was transferred to the American Physical Society. A second series was then begun, the January, 1913, number being designated Volume I., Number 1, Second Series. (An announcement of this transfer will be found on the first page of the new series.)

For advertising rates, address THE PHYSICAL REVIEW, *Ithaca, N. Y.* Change of copy in standing advertisements should be sent direct to the printers, THE NEW ERA PRINTING CO., *Lancaster, Pa.*

Contributors to the REVIEW are referred to page two of the advertisements for further information.

Permission is given to republish any article appearing in the REVIEW, provided proper credit is given.

Address Correspondence to

THE PHYSICAL REVIEW, ITHACA, N. Y.

Second Series. *December, 1916* *Vol. VIII., No. 6*

THE

PHYSICAL REVIEW.

THE DIELECTRIC CONSTANT OF AQUEOUS SOLUTIONS.

By Elmer A. Harrington.

THE principle of the method for the determination of dielectric constants consists in comparing, by the application of the telephone in the Wheatstone bridge, the capacity of a dielectric trough with that of a glass condenser of variable capacity. This apparatus was first used for these purposes by Nernst,[1] who found that liquids of conductivities as large as 2.10^{-10} could be measured quite accurately. With much larger conductivities the disturbances due to polarization, as well as the difficulties of a comparatively complete compensation of conductivity, become very great.

Since the effect of a polarization capacity, like that of a resistance connected in parallel with a condenser, decreases as the frequency increases, we have here, as a means of avoiding these difficulties, the application of an alternating current of high frequency,[2] which one easily obtains from the oscillatory discharge of a condenser through a self-induction.

The Apparatus.

The arrangement of the apparatus is shown in the accompanying figure (Fig. 1). It consists essentially of two systems, the first of which is really a sending system, while the second may be thought of as a receiving system.

I is a large induction coil, the oscillations being produced by a Wehnelt interrupter. The spark-gap S charges the two equal and symmetrically-placed condensers C_1 and C_2. P_1 and P_2 are comparatively loosely coupled self-inductions made up of a few turns of large wire about coaxial cylinders. P_2 excites the Wheatstone bridge, which consists of two self-

[1] Nernst, Zeit. f. phys. Chem., 14, p. 622, 1894.

[2] Nernst, Wied. Ann., 60, 600, 1897.

inductions p_1 and p_2, and of two variable condensers of capacity c_1 and c_2.

Since the frequency of the current is of the order of 1.10^6 per second it is necessary to use a wave detector *W.D.* and a battery *B* with the telephone *T* to show a balance in the bridge. A detector was first applied in this connection by Nernst.[1] *K* is a blocking condenser (3.2 microfarads), placed in the detector circuit as indicated.

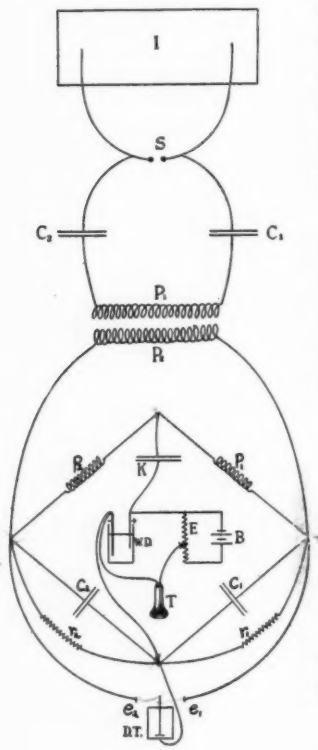


Fig. 1.

The dielectric trough *D.T.*, or condenser consists of a metal disc fixed at a certain distance from the bottom of the vessel, contains the liquid under investigation and may be connected in parallel first with c_1, and then with c_2, by means of the contacts e_1 and e_2.

The Transmitting Circuit.

An interrupter of the Wehnelt type was used in the primary circuit as it produced the most regular and uniform strengths of oscillations in the transmitting circuit.

An adjustable spark-gap *S* bought from the Clapp-Eastham Co., of Cambridge, was found to be most efficient and regular.

The condensers C_1 and C_2 are made up in such a manner as to minimize all brush discharges. The capacity of each condenser is 0.012 microfarad, and since they are connected in series, the capacity of the system is 0.006 microfarad.

The self-inductions P_1 and P_2 consist of 16 turns of large copper wire about coaxial cylinders of 19 cm. length and of 9 cm. and 13 cm. diameter respectively. Using the Fleming-Anderson bridge method of measuring self-inductions,[2] the following values were obtained:

$$P_1 = 1.5 \cdot 10^4 \text{ cm.}, \qquad P_2 = 2.6 \cdot 10^4 \text{ cm.}$$

The maximum mutual induction between these two coils was found to be $M = 1.15 \cdot 10^4$ cm. The coefficient of coupling is, therefore,

$$k = \frac{M}{\sqrt{P_1 P_2}} = 0.58.$$

[1] Nernst, Ann. d. phys., 15, 836, 1904.

[2] Fleming, Wave Telegraphy, p. 143.

The mutual induction can be decreased by sliding P_1 along the common axis, but the best results are obtained when the ends of the helices are just even; the minimum in the telephone is then sharper and any noise that may be heard in the telephone more nearly disappears.

THE WHEATSTONE BRIDGE.

Self-Inductions.—The self-inductions p_1 and p_2 are made equal because this theoretically simplest case is found to be the most advantageous one experimentally. Each consists of 50 turns of insulated wire about a wooden cylinder 9 cm. in diameter, forming a coil 10 cm. long. The inductances, according to the Fleming method, are

$$p_1 = p_2 = 2.27 \cdot 10^5 \text{ cm.}$$

The coils are placed with their axes vertical and about 46 cm. apart. No mutual induction between the two coils could be detected.

Measuring Condensers.—The variable condensers c_1 and c_2 (Fig. 5), are similar to those used by Turner,[1] but important modifications have been introduced. Each is made up of three accurately planed brass plates, of which the two outer ones are metallically connected by means of a brass strip. Thus the outer plates play the part of the front plate in the old model, while the inner plate forms with these a double condenser, and at the same time it is protected from the influence of surrounding conductors. The inner plate is connected with one end of the coil P_2, so that its potential is much higher than that of the outer plates, whose potential is always nearly that of the earth.

The dimensions of the brass plates are: length, 19.95 cm.; height 7.23 cm.; thickness, 0.47 cm. The distance between the plates is 0.349 cm., and it is kept constant by four little glass rods of that length. Each plate is held in position by four brass screws (two above and two below), which pass through the plate glass beds (0.8 cm. thick) on which the plates are mounted.

In order to insure good insulation the brass plates do not actually touch the glass bed, but are separated from it by four pieces of glass about 0.1 cm. thick and 0.4 cm. square. The glass rods pass loosely through holes in glass strips 0.2 cm. thick and 0.7 cm. wide, and of the same length as the brass plates, cemented edge-on to the glass beds midway between the brass plates. The glass plates slide along on these glass strips. In this way edge corrections are reduced to a minimum, as only that part of the space between the brass plates is used where the lines of force are fairly straight. Insulation is further improved by

[1] Turner, Zeit. f. phys. Chem., 35, 385, 1900.

raising the glass bed 5 cm. from the table by means of three pieces of plate glass cemented edge-on to the bottom of the bed.

The use of glass for the bed of the condenser is a decided improvement in the apparatus, as glass does not twist and warp as hard rubber does; and the methods described above, of obtaining the best possible insulation are rendered more simple by using nothing but glass and brass in constructing the apparatus.

The glass plates are of optical glass 25 cm. long, 6 cm. wide and 0.3250 cm. thick. Each glass plate is movable between the middle and one of the outer brass plates, and its displacement can be read off the glass scale on the bed by means of the vernier on the glass plate. When the brass plates are exactly parallel, and the glass plates are of uniform thickness, the displacements of the glass plates are proportional to the change of capacity. The displacements are evidently additive, as the double condenser really consists of two condensers connected in parallel; and the capacity of one of them is not affected at al by a change of the other. From the dimensions of these condensers we may calculate approximately their capacity. The minimum capacity is about 100 cm., while the average capacity may be taken as 260 cm.

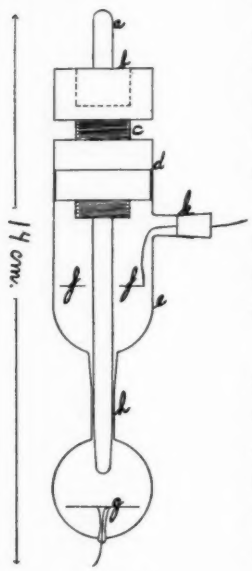


Fig. 2.

These condensers are placed on the table in an end-on position with their ends about 35 cm. apart. At this distance the effect of one condenser on the capacity of the other may be left out of account.

Compensating Resistances.—The compensating resistances r_1 and r_2 are like those used by Turner,[1] in which the distance between the electrodes remains constant, and the resistance is changed by pushing a glass rod into the constriction in the vessel and thus decreasing the area of cross section of the resistance liquid. The details are easily understood from the figure below.

The glass rod (*a*) fits closely in a cork (*b*) in the hard rubber screw (*c*), and yet it is easily displaced; the nut (*d*), also of hard rubber, is fixed in the glass tube (*e*). The electrode (*f*), is a platinum ring with a platinum wire attached; the other electrode (*g*) is fused into the glass at the bottom.

In order to obtain a sufficiently large variation of the resistance, the glass rod must fit as accurately as possible into the narrow part (*h*) of

[1] Turner, Zeit. f. phys. Chem., 35, 385, 1900.

the glass tube. The diameter of the rod is 0.6 cm., while the inner diameter of the tube is about $\frac{1}{2}$ mm. larger. In order to allow a very exact setting when using the smallest resistances, the mouth of the tube (*h*) in the upper part of the vessel is made slightly conical and the rod is given a similarly conical form. The side-neck (*k*) serves to lead in the wire of the electrode (*f*).

The vessel is mounted in a wooden frame in such a way that the lower electrode (*g*) is about 4 cm. above the table. The vessel is then placed about 20 cm. from the measuring condenser. Polarization may be neglected with these comparatively large electrodes. Magnanini solution[1] is used as the compensating liquid on account of its low temperature coefficient. Another advantage of this form of apparatus is that the outer variable capacity is reduced practically to zero.

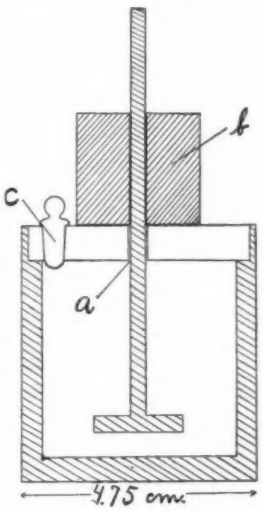


Fig. 3.

Dielectric Trough.—The dielectric trough *D.T.* is a modification of that used by Turner (*loc. cit.*). The figure below shows a cross section of the trough. The sides and bottom are of brass, silver plated inside and nickel plated outside. The cover is of glass, and it fits so well into the top of the trough that the whole trough may be picked up by the cover. In this way all sidewise motion is completely overcome. The hole (*a*) in the center of the cover is enough larger than the brass rod which passes through it, so that the rod does not touch the glass cover, but is held in position by the hard rubber cylinder (*b*) which is cemented to the cover. In the cover there is a second hole, (*c*) through which the liquid to be investigated may be introduced.

With a cover of glass, and a cylinder of hard rubber fastened on the top through which the rod passes easily but not too easily, the errors due to a sidewise movement of the rod in the cover of the trough, or of the cover itself on the top of the trough, are eliminated. The cover is not elastic and it is not affected by the vapor of the liquid in the trough.

The dielectric trough should be filled to two thirds or three fourths of its height. That is, the trough should be filled till no lines of force are drawn into the upper surface of the liquid. This will be the case when the surface of the liquid is in the direction of the lines of force. It is also evident that the trough must be filled to the same height in

[1] Magnanini, Zeit. f. Phys. Chem., 14, p. 622, 1894.

every case. In these experiments 30 c.c. of liquid were always introduced into the trough through the hole (e) by means of a pipette.

As it is difficult when using conducting solutions to keep the temperature of the trough sufficiently constant, it is found convenient to put the trough in a thick-walled brass cylinder, bored out so that the trough fits in snugly but easily (see Fig. 4). On account of the high conductivity of the brass there is practically no difference of temperature between the upper and lower parts, while the large mass of the cylinder gives a regular and slow exchange of heat with the surrounding air. In this way the temperature varies very slowly, and seldom changes more than 0.4°–0.5° during a series of readings. A hole is bored down into the brass and a thermometer placed in it gives the temperature to within 0.1°. The cylinder used is 6.4 cm. long and 7.8 cm. in diameter, the walls being 1.5 cm. thick.

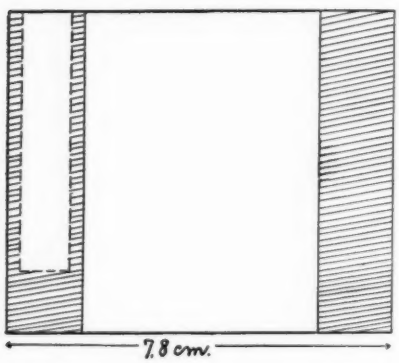


Fig. 4.

The dielectric trough and the brass cylinder are insulated from the table by being placed on a brass disc 5 cm. in diameter cemented to the top of a large piece of glass 7.5 cm. high. Good contact between the bottom of the trough and the disc is very important, because if air is between a condenser of small but finite capacity is introduced. The bottom of the trough and the top of the disc are therefore planed and scraped in order that the area of contact should be as large as possible.

The glass base can be slid from side to side along glass ways so that the rod of the dielectric trough touches the wire e_1 or e_2. In this way the trough can be connected in parallel with the measuring condensers c_1 or c_2, respectively, as the brass disc is always connected by wires to the outer brass plates of these condensers. By means of a glass rod frame e_1 and e_2 are kept in the same positions relatively to c_1 and c_2, and to themselves (it is 6 cm. from e_1 to e_2).

Wave Detector.—The detector used in these experiments is an electolytic detector. The accurate adjustment of the local voltage is made by the use of a potentiometer, E.[1]

Telephone.—A Fritz Köhler telephone of 80 ohms' resistance was selected as the most sensitive for this kind of work. With the electrolytic detector properly adjusted it is possible with this telephone to obtain a

[1] Pierce, Principles of Wireless Telegraphy, Fig. 233, p. 325.

very sharp minimum in which absolutely no noise is heard, even when the dielectric trough contains a liquid of as high conductivity as $1 \cdot 10^{-5}$. Under these conditions it is comparatively easy to set the glass plates of the measuring condensers to within 0.1 mm.

It must be emphasized that extreme sharpness in the telephone is the necessary condition not only for precision, but also for convenience. No determination is to be considered accurate in which the minimum is flat, because it evidently means that somewhere in the bridge something is out of order. Attention must be given to good contact; the existence of a small spark in any part of the bridge is a source of error, as the minimum in the telephone is destroyed and the observation is worthless.

All parts of the apparatus are well insulated and their positions are fixed on the table in order that no change of capacity or self-induction should be introduced. The apparatus is also arranged as symmetrically as possible.

The frequency of the current in the primary circuit and in the Wheatstone bridge may be calculated from the dimensions of the apparatus which have been given. For convenience we may record at this point some of the values in the calculations:

Self-induction in primary $= P_1 = 1.5 \cdot 10^4$ cm.
Capacity in primary $= C = 0.006\ MF = 6 \cdot 10^{-18}$ elec. mag. units.
Self-induction in bridge $= p_1 = 2.27 \cdot 10^5$ cm.
Capacity in bridge $= c_1 = 260$ cm. $= 2.9 \cdot 10^{-19}$ elec. mag. units.
Exciting self-induction $= P_2 = 2.6 \cdot 10^4$ cm.

If N = frequency in primary circuit, and n = frequency in bridge, then

$$N = \frac{1}{2\pi\sqrt{P_1 C}} = 5.4 \cdot 10^5/\text{sec.}$$

and

$$n = \frac{1}{2\pi\sqrt{(p_1 + 2P_2)c_1}} = 5.6 \cdot 10^5/\text{sec.}$$

It is evident that the frequency in the bridge changes with every change in the capacity c, which is produced by moving the glass plates in or out when taking readings; and the compensating resistances have a strong damping effect on the oscillations, whereby the frequency in the bridge is somewhat decreased; but these calculated values give an idea of the order of magnitude of the frequency of the currents used during an experiment.

THEORY.

The condition for silence in the telephone is

$$p_1 : p_2 = c_2 : c_1.$$

When p_1 is made equal to p_2, and c_1 and c_2 are arranged as adjustable condensers, this method enables one to compare the capacity of the dielectric trough with another and thus determine the dielectric constant. The capacity of the dielectric trough is obtained first without and then with the dielectric between its plates. If c is the capacity of the dielectric trough when filled with air, and c' the corresponding value when the trough is filled with the substance in question, of which the dielectric constant is D, then we have

$$D = \frac{c'}{c}.$$

If the substance is a relatively good conductor the current in the condenser circuit not only charges the condenser but also flows through it, and this branch acts as if a non-inductive resistance were connected in parallel with the condenser. Equilibrium in the bridge can be obtained again if a corresponding resistance is connected in parallel with the measuring condensers. Let these variable non-inductive resistances be r_1 and r_2.

The conditions for equilibrium are

$$\frac{r_1}{\sqrt{1 + \omega^2 c_1^2 r_1^2}} : \frac{r_2}{\sqrt{1 + \omega^2 c_2^2 r_2^2}} = p_1 : p_2.$$

In order that there shall be no difference of phase:

$$r_1 : r_2 = p_1 : p_2.$$

From these two equations we get

$$c_1 r_1 = c_2 r_2$$

or

$$c_1 : c_2 = r_2 : r_1 = p_2 : p_1.$$

Thus the capacity does not depend on the frequency.

PRACTICAL METHOD.

In order to eliminate the outer capacity the ratio is taken of the difference of capacities at different distances of the disc from the bottom of the trough when the trough is filled (S) to that when it is empty (s). This ratio is, by definition, the dielectric constant,

$$D = \frac{S_1 - S_2}{s_1 - s_2}.$$

The chief source of error lies in the difficulty with which the correct displacement of the glass plates is obtained. The position of the plate corresponding to a minimum in the telephone is therefore determined

by setting the plate ten times and taking the average of these readings. This is done when the dielectric trough is connected in parallel with c_1, and with c_2. The difference between the two average positions gives the displacement S (or s).

The dielectric constants given below are referred to air, the dielectric constant of which is taken as unity.

RESULTS.

The object of these experiments is to find out the effect of change of concentration on the dielectric constant of aqueous solutions. The substances selected for investigation are non-electrolytes, and are either liquids, which can be easily purified by fractional distillation, or solids, which can be obtained in a very pure state. All readings were taken at 18.0° C.

As water has a very high dielectric constant it seemed advisable to use some liquid, which has a dielectric constant of about 10, as a standard with which to compare the water solutions. This method is not only more convenient but the percentage errors, due to the use of small displacements of the glass plates in the measuring condensers, are thereby diminished. The liquid chosen as the standard is ethyl bromide, because it is cheap, easily purified, not very volatile, does not absorb water readily, and has a dielectric constant of about 9.5.

The dielectric constant of ethyl bromide was found by comparing it directly with air. In this case S represents the displacement of the glass plates when the dielectric trough is filled with ethyl bromide, and s the corresponding displacement when the trough is filled with air. But in the later experiments, when ethyl bromide is used as the standard, s represents the displacement of the glass plates when the trough is filled with ethyl bromide, while S is the corresponding displacement when the trough is filled with the solution in question.

ETHYL BROMIDE.

The so-called "chemically pure" ethyl bromide, free from ether, was distilled twice in the ordinary way, and then distilled over phosphorus pentoxide. The middle part (probably nine-tenths) of the distillate, which boiled over at about 38.2°, was used in the following experiments.

Air.	Ethyl Bromide.
$s_1 = 1.205$	$S_1 = 3.791$
$s_2 = 1.206$	$S_2 = 3.799$
$s_3 = 1.207$	$S_3 = 3.799$
$s_4 = 1.205$	$S_4 = 3.796$
$s_5 = 1.211$	$S_5 = 3.807$

Air.	Ethyl Bromide.
$s_6 = 1.211$	$S_6 = 3.811$
$s_7 = 1.214$	$S_7 = 3.812$
$s_8 = 1.210$	$S_8 = 3.806$
$s_9 = 1.207$	$S_9 = 3.802$
$s_{10} = 1.216$	$S_{10} = 3.814$
$s_{11} = 5.243$	$S_{11} = 41.865$
$s_{12} = 5.240$	$S_{12} = 41.851$
$s_{13} = 5.248$	$S_{13} = 41.939$
$s_{14} = 5.248$	$S_{14} = 41.925$
$s_{15} = 5.248$	$S_{15} = 41.951$
$s_{16} = 5.239$	$S_{16} = 41.856$
$s_{17} = 5.235$	$S_{17} = 41.828$
$s_{18} = 5.234$	$S_{18} = 41.782$
$s_{19} = 5.247$	$S_{19} = 41.882$
$s_{20} = 5.236$	$S_{20} = 41.847$

$D = 9.443.$

Five months later another determination of the dielectric constant of ethyl bromide was made, and the following result was obtained:

$$D = 9.445.$$

The average value of D—9.444—was used in calculating the dielectric constants of the aqueous solutions.

WATER.

Ordinary distilled water was redistilled twice—over alkaline and acid permanganate solution. This pure water was then compared with the standard, ethyl bromide.

Ethyl Bromide.	Water.	Ethyl Bromide.	Water.
$s_1 = 7.875$	$S_1 = 59.418$	$s_{16} = 3.988$	$S_{16} = 26.921$
$s_2 = 7.888$	$S_2 = 59.495$	$s_{17} = 4.007$	$S_{17} = 27.119$
$s_3 = 7.623$	$S_3 = 57.216$	$s_{18} = 3.971$	$S_{18} = 26.904$
$s_4 = 7.689$	$S_4 = 57.678$	$s_{19} = 3.972$	$S_{19} = 26.947$
$s_5 = 7.880$	$S_5 = 59.370$	$s_{20} = 3.970$	$S_{20} = 26.786$
$s_6 = 7.782$	$S_6 = 58.610$	$s_{21} = 3.978$	$S_{21} = 26.726$
$s_7 = 7.685$	$S_7 = 57.770$	$s_{22} = 4.001$	$S_{22} = 27.118$
$s_8 = 7.378$	$S_8 = 55.132$	$s_{23} = 4.016$	$S_{23} = 27.136$
$s_9 = 7.607$	$S_9 = 56.979$	$s_{24} = 3.996$	$S_{24} = 27.106$
$s_{10} = 7.900$	$S_{10} = 59.595$	$s_{25} = 4.032$	$S_{25} = 27.288$
$s_{11} = 7.725$	$S_{11} = 58.191$	$s_{26} = 4.040$	$S_{26} = 27.224$
$s_{12} = 7.597$	$S_{12} = 57.064$	$s_{27} = 4.088$	$S_{27} = 27.895$
$s_{13} = 7.888$	$S_{13} = 59.547$	$s_{28} = 4.027$	$S_{28} = 27.145$
$s_{14} = 7.704$	$S_{14} = 57.989$	$s_{29} = 3.986$	$S_{29} = 26.988$
$s_{15} = 7.620$	$S_{15} = 57.253$	$s_{30} = 3.981$	$S_{30} = 26.903$

$D = 78.73.$

Tap water was investigated, and the dielectric constant was found to be 78.5, a value which may be considered the same as that of pure water.

This dielectric constant is entirely independent of the conductivity. But the sharpness of the minimum in the telephone is greatly reduced by an increase of conductivity, and a corresponding reduction in the accuracy of the result is thereby produced.

Moreover, the conductivity of the pure water is considerably increased by pipetting the water into the dielectric trough, so that the conductivity of the water during an experiment is probably about $2 \cdot 10^{-6}$ absolute units.

Tables like the preceding were obtained for the following solutions, but they are too long for reproduction here. The method of calculating the results is exactly the same.

Sugar Solution.

Large crystals of Kahlbaum's purest saccharose were dissolved in pure water and the molar concentration was varied between 0.1 and 1.4. The dielectric constant was found at the different concentrations as follows:

Concentration.	Dielectric Constant.
0.1	77.64
0.2	76.73
0.4	75.53
0.5	75.05
0.6	74.46
0.7	73.84
0.9	72.52
1.0	71.84
1.2	70.36
1.4	68.67

From these results it is evident that an increase of the concentration of the sugar solution causes a decrease of the dielectric constant. This is as it should be, as the dielectric constant of sugar is not very high.

Urea Solution.

Kahlbaum's best "Harnstoff" was taken without any further purification and dissolved in pure water to give solutions of concentrations which varied from 0.5 molar to 3.0 molar.

Concentration.	Dielectric Constant.
0.5	80.22
1.0	81.51
1.5	82.81
2.0	83.98
2.5	85.16
3.0	86.17

From these data we see that an increase in the concentration of the

urea solution gives an increase in the dielectric constant. Such a result is contrary to all expectation, and, so far as I know, it is unique.

METHYL ALCOHOL.

Absolute methyl alcohol, free from acetone (from Eimer and Amend), was distilled over lime; and the middle part of the distillate (at least 90 per cent.), which boiled over at about 64.4°, was used in the following experiments. The amount of water with which the methyl alcohol was mixed was varied in six steps from 0 per cent. to 100 per cent.

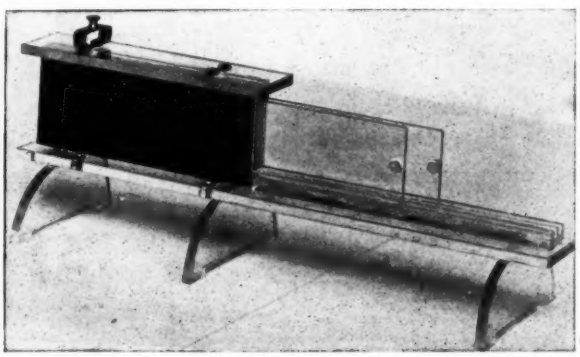


Fig. 5.

Concentration.	Dielectric Constant.
100.0	33.78
84.0	40.96
75.9	45.31
48.0	57.44
33.1	64.47
17.4	71.11

It is evident from these results that a nearly linear relation exists between the amount of water added to the methyl alcohol and the increase in the dielectric constant thereby produced.

CONCLUSIONS.

The Nernst method for the determination of the dielectric constant of liquids has been carefully examined; and the apparatus, particularly the measuring condensers and the dielectric trough, has been perfected so that it is now possible to measure accurately the dielectric constant of liquids whose conductivity is as high as $1 \cdot 10^{-5}$ absolute units. This is probably the highest conductivity for which consistent values of the dielectric constant have ever been obtained.

With this improved apparatus the effect on the dielectric constant of

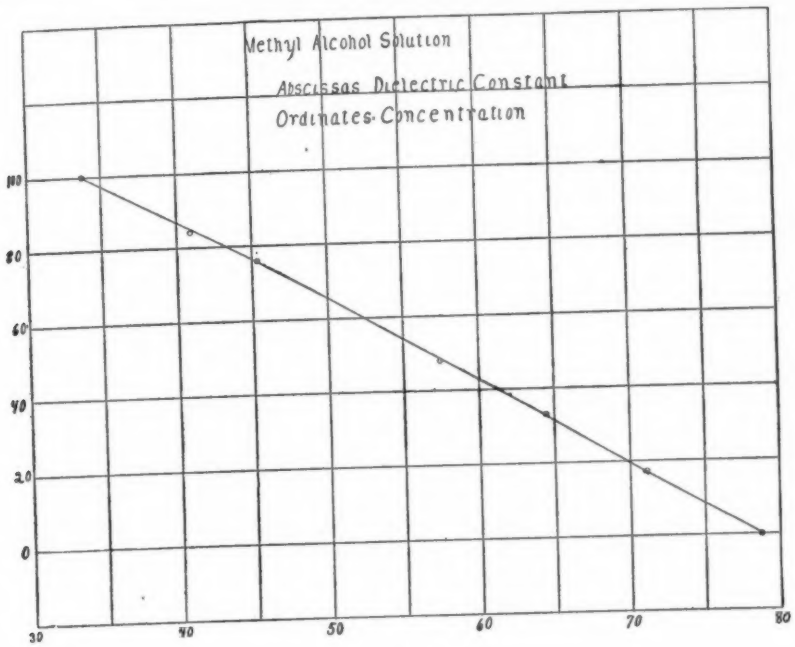

Methyl Alcohol Solution
Abscissas Dielectric Constant
Ordinates Concentration
100
80
60
40
20
0
30
40
50
60
70
80

Fig. 6.

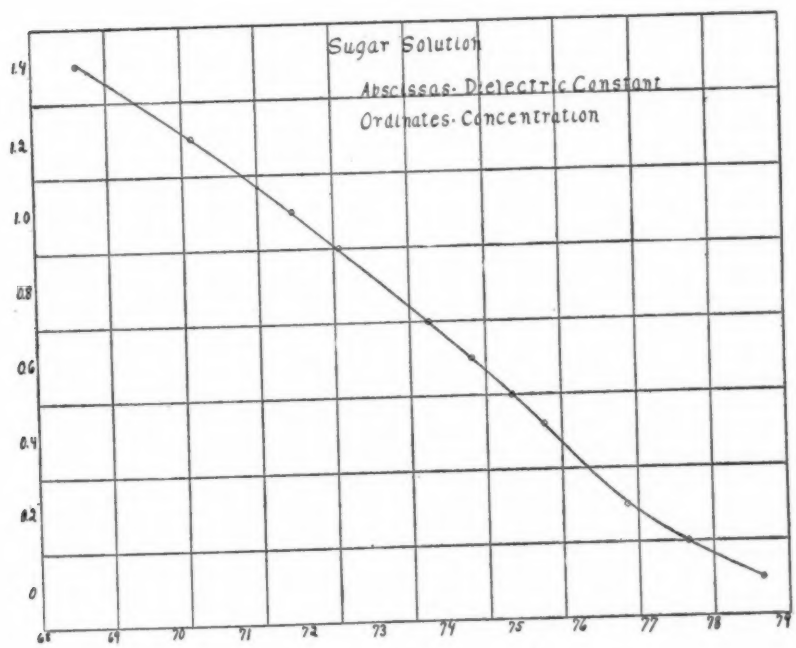

Sugar Solution
Abscissas Dielectric Constant
Ordinates Concentration
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0
68
69
70
71
72
73
74
75
76
77
78
79

Fig. 7.

an increase of concentration of aqueous solutions of sugar, urea, and methyl alcohol respectively has been investigated; and the relation is bound to be nearly linear.

The author takes this opportunity to express his gratitude to Clark University for the apparatus placed at his disposal, and particularly to Professor Webster for many valuable suggestions in carrying out the research.

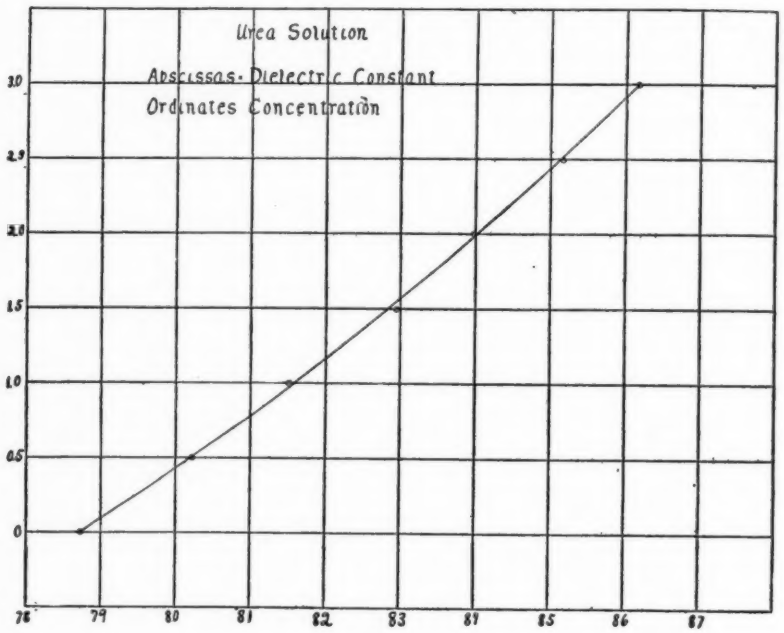


Fig. 8.

CLARK UNIVERSITY, WORCESTER, MASS.,
June 26, 1915.

THE EXISTENCE OF A SUBELECTRON?

BY R. A. MILLIKAN.

1. THE HISTORY OF THE IDEA OF A UNIT CHARGE.

IT was in the year 1833 that Faraday's discoveries in electrolysis first suggested the existence of an elementary electrical charge, and first made possible a rough estimate as to its value. This estimate was first carried through in 1874 by G. Johnstone Stoney,[1] who first used the word *electron*[2] as a name for the "natural unit of electricity" and who published as its value $.3 \times 10^{-10}$ E.S. units, a value obtained from electrolytic determinations of the product Ne and from kinetic theory estimates of N, the number of molecules in a gram molecule. These kinetic theory estimates vary ten fold, but if we take the value which was most current about 1900, namely that given in O. E. Meyer's well-known book[3] we obtain by Stoney's method $e = 2 \times 10^{-10}$.

The laws of Faraday were not regarded, however, even by the keenest of intellects as demonstrating in general the atomic structure of electricity, for it was entirely logical to attribute the exact multiple relations shown by the charges appearing in electrolysis to properties of the atoms carrying these charges rather than to an atomic property of electricity itself. This was the course actually taken by Maxwell,[4] who expressed himself positively as opposed to a general atomic theory of electricity. Furthermore, Faraday, Helmholtz[5] and Kelvin[6] all showed clearly that they did not regard the apparent ionic charges existing in electrolytes as necessarily existing in separate elements on charged metals. Indeed a sharp distinction was practically universally made up to 1900 between the phenomena of metallic and those of electrolytic conduction.

[1] Trans. Roy. Dublin Soc., 4, p. 582, 1891. Also Phil. Mag., 1881, p. 385.

[2] The most authoritative of modern writers such as Thomson, Rutherford, Richardson, Campbell, etc., have been careful to retain the original significance of the word electron instead of using it to denote solely the free negative electron or corpuscle of Sir J. J. Thomson. These writers all speak of positive as well as negative elections although the mass associated with the former is never less than that of the hydrogen atom.

[3] Die Kinetische Theorie der Gase, 1899. The number of gas molecules per c.c. is here given as 6×10^{19} which corresponds to $N = 1.34 \times 10^{24}$.

[4] Electricity and Magnetism, 1873, p. 380 and 381.

[5] Helmholtz's Wissenschaftliche Abhandlungen, Vol. 3, p. 69.

[6] Nature, Vol. LVI., p. 84, 1897.

The experiments made at the Cavendish Laboratory[1] about 1900 by Townsend, Thomson, Zeleny, Rutherford, H. A. and C. T. R. Wilson and others simply showed that gaseous conduction is of the same kind as electrolytic conduction, but did not throw any new light on the nature of metallic conduction. They did, however, give great stimulus to the atomic theory of electricity and caused it to become the prevalent mode of interpreting electrical phenomena. They brought to light the existence of a body, J. J. Thomson's corpuscle, for which the value of e/m was 1/1830 of that found on the hydrogen ion in electrolysis. Townsend,[2] J. J. Thomson,[3] H. A. Wilson,[4] Przibram,[5] Millikan and Begeman,[6] Ehrenhaft[7] and Broglie[8] in succession made rough determinations or estimates of the average charge appearing on gaseous ions and found it equal, within the limits of uncertainty (say one or two hundred per cent.), to the value estimated for the univalent ions in electrolysis.

2. Isolation of Individual Droplets and the Measurement of Their Charges.

None of the methods used by any of these observers were capable, however, of yielding anything more than the *mean* ionic charge. That the ionic charges in both solutions and in gases were all alike was commonly assumed but could not be proved. Ehrenhaft, in a paper read at the Naturforschersammlung zu Königsberg in Sept., 1910, made a very clear statement of this defect in his own attempted determination of e, and asserted that it inhered also in the work of all other observers. *As a matter of fact, however, I had had the good fortune to find a way of removing this limitation entirely more than a year earlier, viz., in the spring and summer of* 1909.[9] This had been done by isolating in a vertical electric field individual charged water droplets and determining the amount of electricity carried by each drop by measuring (1) the speed under gravity, (2) the speed under the combined action of the field and gravity. The following is a quotation from this article written October 9, 1909:[10] "It is an exceedingly interesting and instructive experiment to

[1] J. J. Thomson's Conduction of Electricity through Gases, 1906.

[2] Proc. Cambridge Phil. Soc., 9, p. 244, 1897.

[3] Phil. Mag., 46, p. 528, 1898.

[4] Phil. Mag., 5, p. 429, 1903.

[5] Phys. Zeit., Juli, 1907.

[6] PHYS. REV., XXVI., p. 198, 1908.

[7] Phys. Zeit., 10, p. 308, 1909.

[8] Le Radium, 6, p. 203, 1909.

[9] This method and the results were reported at the British Association meeting in Winnipeg in August, 1909, being placed upon the program as an additional paper. They were first published in brief in the PHYSICAL REVIEW, Vol. 29, p. 260, 1909, and in full in the Phil. Mag. for Feb., 1910, Vol. 19, p. 209.

[10] Phil. Mag., 19, p. 219.

watch one of these drops start, and stop, or even reverse its direction of motion, as the field is thrown off and on. I have often caught a drop which was just too light to remain stationary and moved it back and forth in this way four or five times between the same two cross-hairs, watching it first fall under gravity when the field was thrown off, and then rise against gravity when the field was thrown on. *The accuracy and certainty with which the instants of passage of the drops across the cross-hairs can be determined is precisely the same as that obtainable in timing the passage of a star across the cross-hairs of a transit instrument.*

"Furthermore, since the observations upon the quantities occurring in equation (4) are all made *upon the same drop* all uncertainties as to whether conditions can be exactly duplicated in the formation of successive clouds obviously disappear. There is no theoretical uncertainty whatever left in the method unless it be an uncertainty as to whether or not Stokes' law applies to the rate of fall of these drops under gravity. The experimental uncertainties are reduced to the uncertainty in a time determination of from three to five seconds, when the object being timed is a single moving bright point."

A comparison of the charges obtained by this method showed that within the limits of experimental error, they were 2, 3, 4, 5 and 6 times a particular charge which obviously had to be the smallest charge which appeared in the gaseous ionization which I was studying. The value of this charge, according to the simple mean of my measurements was 4.70×10^{-10} electrostatic units.

Professor Ehrenhaft a year later published the above mentioned Königsberg paper[1] in which he discussed my 1909 work and claimed that I had not determined the charges on individual particles, but that he had now devised a method of doing so. His words are: "Bei dieser ersten Ausführung [that of 1909] war es mir nicht gelungen an ein und demselben Metallteilchen elektrische Beobachtung und Fallbeobachtung hintereinander zu machen. Erst die hier eingeschlagene Weg gestattet, bis on die Grenze der Ultramicroscopie, die Geschwindegkeit der Steigbewegung eines Einzelteilchens unter Einfluss einer greigneten Spannung und so dann *an eben und demselben Teilchen* die Fallgeschwindigkeit desselben partikels unter blossem Einflusse der Erdschwere bei Kurzgeschlossenem Kondensator zu messen."

Professor Ehrenhaft's new arrangement, then, and his new method of

[1] Its first appearance in print was in somewhat modified form in the Juli 15, 1910, number of the Phys. Zeit., p. 619, under the title "Ueber eine nene Methode zur Messung von Elektrizitätsmengen an Einzelteilchen deren Ladung die Ladung des Elektrons erheblich unterschreiten, etc."

observation were identical in every essential particular with those which I used in the paper which he was criticizing, but quite distinct, as he himself says, from anything which he had used in his earlier work. For, prior to the 1910 paper[1] Professor Ehrenhaft had never used a vertically directed electric field[2] and hence, as he correctly pointed out, he had not been able to find the charge on a particular particle. The reason which he assigned for contending that I too had not determined the charges on individual particles, was that in my summary of results, I had taken my values of $2e$, $3e$, etc., from observations in each case upon several drops which carried the charges $2e$, etc. I had done this, however, only for such drops as were obliged, because they were exactly balanced by exactly the same electric field, and fell at the same rate under gravity, to be of exactly the same size and to carry exactly the same charge. Balanced drops having different charges fell with totally different speeds when the field was thrown off, and therefore, never came into consideration. What I actually did was neither more nor less than is always done in obtaining an accurate measurement of any physical magnitude, for example, a length, namely to make exactly the same measurement several times over, and then take a mean solely *for the sake of diminishing the error in reading the measuring instrument.* This instrument was in my case a stopwatch. There was not the slightest reason for considering the fluctuations which Professor Ehrenhaft found in my measurement of e as arising from varying values of the ionic charge, since they were no larger than the necessary fluctuations in a stopwatch measurement of an interval from 2 to 5 seconds in length. Had I worked out e for each individual reading and then taken the mean my result would of necessity have come out exactly as it did. The point raised has to do, therefore, merely with the way in which I tabulated my data, not at all with the way in which I made my measurements, *which were in fact measurements upon the charge carried by individual particles.*

The reason for this effort to find variations in my measurements of the charges carried by different ions lay in the fact that, as soon as in 1910 Professor Ehrenhaft had changed from the de Broglie method of handling his metal particles to the method which I had used with the water drop, and which alone made possible the determination of the charge on a single particle, he found that these charges, as he determined

[1] This appears also in somewhat modified form in the Wiener Berichte of the 12th of May, Bd. CXIX., abt. II*a*, 1910, but this publication does not seem to have appeared till December, 1910, at least it is not noted in "Naturae Novitates" before this date.

[2] Indeed in the 1909 work referred to above he had used precisely the arrangement and method of observation described fully and used in 1908 by de Broglie in his study of charged metal particles coming from arcs or sparks between metal electrodes. See Compte Rendu, 1908, pp. 624 and 1010.

them, showed wide irregularities. These he interpreted as indicating that there is no elementary electrical charge, the smallest charge appearing in preceding work on solutions and gases being nothing but a statistical mean, made up of widely varying charges. The only experiment which had appeared which seemed to negative such a view were these of mine on the charges on water droplets, hence it was necessary to make it appear that these also showed fluctuations.

3. General Proof of the Atomic Structure of Electricity.

In April, 1910, three months before the first appearance in print in the Physikalische Zeitschrift of this paper of Ehrenhaft's, which seemed to undermine all the rapidly spreading views as to the granular structure of electricity, I read before the American Physical Society the paper[1] which seemed to me to establish in a perfectly general way the view that all electric charges, whether on ions or on large bodies, insulators or conductors, are simply an assemblage of elementary electrical specks or atoms all of which are exactly alike. The essential element in this proof lay in these three facts not brought out by any other experiments until 2 or 3 years later: (1) that the ionic charges obtained by capturing ions from gases on any kind of a body are all exactly alike or else small exact multiples of a definite charge; (2) that the static charges residing on all kinds of bodies from insulators up to conductors and put there by frictional or other processes are always exact multiples of this smallest ionic charge. (3) That the direct detachment of negative electrons from the drop by the incidence of X-rays upon it produces the same change in charge as the capture of an ion.[2]

So long as a charged droplet remains constant in shape and size the change in its speed in a given electrical field caused by the capture by the drop of one or more ions is a measure of the charge carried by the captured ion or ions. *These changes in speed were found to be all exactly alike or else exact small multiples.*

Again if the total speed produced in the charged drop by throwing on the given electrical field is found to be always an exact multiple of the smallest change in speed produced by the capture of ions, then the original charge, produced by friction or otherwise, must be built up out of these smallest ionic charges. *This relation was found to be in every case very exactly fulfilled.*

Finally, if the change in speed produced by letting X-rays or ultra-

[1] This paper appeared in print in abstract in Phys. Rev., 31, p. 92, July 15, 1910; also in Science, XXXII., p. 436–443, Sept., 1910; also in Phys. Zeit., XI., p. 1097–1109, 1910. For a more complete article see Phys. Rev., XXXII., pp. 351–397, April, 1911.

[2] See The Electron. Its Isolation and Measurement, etc. University of Chicago Press, 1917.

violet light fall upon the particle and detach negative corpuscles from it is the same as that produced by the capture of ions, then the ionic charge must be the same as the charge carried by the corpuscle or beta particle. Every one of these relations was carefully studied in the winter of 1909 and 1910 and in the paper read in April, 1910, the conclusion was announced that these experiments furnished indubitable proof of the most general and unimpeachable kind of the atomic structure of electricity. This conclusion was drawn only after four months of continuous experimenting from December, 1909, to April, 1910,[1] on drops of many kinds of materials, some of which were good conductors like mercury, some semi-conductors like glycerine, some very bad conductors like oil. Furthermore, these drops were often held under observation for four and five hours at a time, during which period scores of changes in charge in a given drop were produced both by the capture of ions and by the discharge of negative corpuscles from the drop by the direct incidence of X-rays. When it was desired to avoid this direct loss of electrons by the drop, lead screens were arranged so that the drop itself would not be illuminated by the rays although the gas underneath it was ionized by them.[2] We found, too, in 1910 that when we worked at very low gas pressures, changes in charge due to the capture of ions became very infrequent on account of the scarcity of ions, even when strong X-rays were passing between the plates, while changes due to the direct ejection of electrons from the drop by the direct incidence of the rays were as frequent as ever, the result being that at low pressures it is very easy to make the charge on the drop change toward greater positiveness, but next to impossible to make it change in the opposite direction. I did not in this first work, reported in 1910, discharge electrons from the drop by ultra-violet light, but I did discharge them by the direct incidence of both X-rays and gamma rays which were known from J. J. Thomson's and Lenard's work to discharge negative bodies having the same value of e/m as those discharged by ultra-violet light. Joffé[3] and Meyer and Gerlach[4] made in 1913 the first careful study of this case itself, using the balanced drop method precisely as I had used it in 1909 and 1911[5] and found that when they changed the charge on their drops by discharging corpuscles from them by ultra-violet light, they obtained the same sort of exact multiple relationships between the charges as I had found when I produced the changes either by capturing ions, or by discharging corpuscles from the drops with X-rays

[1] See PHYS. REV., 32, p. 360.

[2] See Phil. Mag., June, 1911, p. 757.

[3] Setz. Ber. d. Konig. Bayer, Akad. der Wiss., Feb., 1913.

[4] Arch. de Genève (*d*), 35, p. 398, 1913. See also Ann. der Phys., 45, p. 177, 1914.

[5] Phil. Mag., Feb., 1910, and June, 1911.

or gamma rays. Joffé's and Meyer and Gerlach's real contribution in these papers consisted in showing that the discharges of electrons by ultra-violet light come at irregular intervals and in making important measurements on the mean length of these intervals, called Aufladungszeiten by Joffé and Verzögerungszeiten by Meyer and Gerlach. In addition they check in every particular and very convincingly my conclusions as to the exactness of the multiple relationship which is found between the charges which can be placed upon a metallic droplet.[1]

Unfortunately even when Professor Ehrenhaft made his Königsberg address in Sept., 1910, he knew nothing whatever of this multiple relationship, for he had made no quantitative study of the phenomena of change of charge and he had not yet seen my paper. In all the work reported in 1910, and for that matter in all so far as I can discover which is reported prior to 1914, he records only the moving of a single particle up and back once, and holding it under observation at most a minute, precisely as I had described doing in 1909. The stage to which his experiments had progressed in 1910 can best be seen from the following note added in proof to the before mentioned fifty-two page paper in the Wiener Berichte which appeared in December, 1910, six months after I had read before the American Physical Society the paper in which I gave most elaborate proof of the multiple relationship between charges and described the keeping of a droplet moving up and down between my plates for five hours at a time, during which time I had forced it scores of times to change its charge by the capture of ions or the loss of negative electrons.

"Verfasser ist im Begriffe, mit Hilfe eines die Zeit registrierenden Dreihebelstiftschreibers von Siemens & Halske die beschriebene Messmethod an demselben Teilchen zu wiederholten Malen durchzuführen, um so den zeitlichen Ladungszustand eines und desselben Partikels zu verfolgen. Es gelang dies bis zu vermal and erwies eine ganz ausserordenliche Präzision der Methode. Es scheint vielfach ein kontinuierliches Entladen der Parikel stattzufinden, dies jedoch nach Bruchteilen des Elektronenwertes. Die Resultate, welche vorliegende Schlüsse erhalten, werde ich in diesen Berichten veröffentlichen."[2]

[1] For accurate measurement of the multiple relations between charges, it is best to measure the two speeds, v_1 and v_2, rather than to try to find the field strength at which the v_2 speed is about zero. Accordingly, for the sake of greater precision of measurement I very early discarded the balanced drop method which Ehrenhaft and Joffé and Meyer and Gerlach have so largely used. This accounts quite largely for the greater consistency of my data.

[2] In other words, Professor Ehrenhaft promises to do with his particles precisely what he had found in his review of my 1909 work, which he criticizes in this article, that I had done with my water drops. I had even in that work observed the change in charge, though I did not discuss it in the 1909 paper. De Broglie had observed it in 1908 (C. R., 146, pp. 624

This quotation is introduced merely to explain how it could happen that Professor Ehrenhaft placed such an interpretation as he did upon his observations of 1910. These showed very large irregularities (Schwankungen) in the values of the charges carried by different particles. He focused his attention upon these Schwankungen and concluded, first, that different ions had different charges and, second, that some of these charges were very much lower than 4.5×10^{-10}, the supposed value of the electron. Had Professor Ehrenhaft known of the exact multiple relationships brought to light by the above experiments he could scarcely have put such an interpretation as he did upon his own results, *for it is in this relation that the unimpeachable evidence that electrical charges are, in fact, all built up out of one and the same sort of unit charges, is found.* In the last six years of experimenting, though scores of persons have repeated my experiments with various modifications, no one, save Konstantinowsky (see below), not even Professor Ehrenhaft himself, has ever observed any departure from the exact multiple relationship which I first pointed out. And, until such a departure is found, it seems to me that there can be no scrap of evidence for the existence of electrical charges smaller than that of the electron, for some of the changes in any series of charges carried by a particle are always due to the capture of ions, and the multiple relationship means that all the other charges appearing in the experiment are multiples of this ionic charge.

4. The Essential Elements in the Droplet Method of Determining the Absolute Value of *e*.

It would, however, be very unfortunate if the charges on different drops could not be reduced to a common measure, *i. e.*, if an absolute determination of *e* could not be made. But my experiments[1] showed that this reduction can, in fact, be made with extraordinary consistency if we adopt the only procedure which it is legitimate to adopt in comparing the velocity of the charged body in a given electric field with its speed under a known force such as *mg*. For this comparison cannot be made unless we know both the mass *m* of the particle and the size of the surface *S* which it opposes to the resistance of the medium, and only then provided we know also the relation between the force acting, the

and 1010, 1908). In spite of the situation revealed in this note, Professor Ehrenhaft in 1914, in reviewing the history of this field of study writes as follows (Wien. Ber., CXXXIII., Feb., 1914, p. 73; also Ann. der Phys., 44, p. 670, 1914): "Die Umladung des Partikels erfolgt am besten durch Ionisierung der Luft im Kondensator. Solche Umladungen habe ich schon im April 1910 konstatiert und im Anhange an meine Abhandlung mitgeteilt. (This is the footnote given above.) Etwa ein halbes Jahr später hat Millikan ebenfalls auf diese Erscheinung bei seinen grössern Ölkugeln hingewiesen."

[1] PHYS. REV., 2, p. 109, 1913; 32, p. 393, 1911.

speed produced by it and the surface exposed to the drag of the medium. This relation we know exactly, both from the theory of Stokes and from the experiments of Arnold, Phil. Mag., 22, 755, 1911, *when and only when the inhomogeneities of the medium are negligibly small compared with the size of the particle.* There is but one possible way, then, to determine *e*, namely *to find the limit toward which the apparent value of e, on the assumption of Stokes's law, approaches as the size of the drop or the pressure of the gas is increased so as to approach the conditions assumed in Stokes's theory and realized in Arnold's experiments.* When this is done, absolutely all irregularities in the measurements disappear, and *e* comes out with extraordinary constancy as my results already published show,[1] and as results recently taken and given below show still more clearly even when the range of drop-radii is extended so as to overlap that in which Ehrenhaft works.

What he found was that when he computed *e* by the aid of the assumption of the validity of Stokes's law for the very minute drops with which he worked he got large irregularities, and these he interpreted as variations in the ionic charge. Mr. Fletcher and I pointed out that such irregularities were to be expected because of Brownian movements[1] when a very short distance of rise and fall was used and when the times of rise and fall were observed but once, as had been the case in Ehrenhaft's experiments. We further showed experimentally that the Brownian movements did account under conditions like those used by him, for just such irregularities as he observed. Furthermore, we suggested that the fact that his mean values fluctuated about a number which was too small for *e* when and only when he was working with very heavy metals, platinum, gold, and mercury, was probably due to the fact that his actual particles were of irregular shape, or else oxides or other compounds of much less mean density than that which he assumed. In any case since he neither got then, nor yet gets, any consistency in the value of *e* obtained with different drops *and yet in every case changes his charge by the capture of precisely the same ions* which my experiments show always carry exactly the same charge, it is obviously absurd to assume that these ionic charges take on one value when they are caught by one kind of a drop and another value when caught by another kind of a drop. *His difficulty had of necessity to be looked for in a wrong assumption as to the shape, or density, or size, or law of motion of his particles.*

5. THE NEW EVIDENCE.

Although Professor Ehrenhaft did not admit the validity of our evidence it was generally considered as settling the matter,[2] even Dr. Karl

[1] Phys. Zeit., 12, p. 161, 1911. See also PHYS. REV., 32, p. 393, 1911.

[2] See Pohl's "Bericht über e," Jahrbuck der Radioactivitat und Elektronik, VIII., p. 431.

Przibram who had collaborated with Professor Ehrenhaft and at first adopted his point of view writing me that although his work in this field had "commenced with such a grievous mistake it was now (1912) in good agreement" with mine.

Very recently, however, Professor Ehrenhaft[1] and two of his pupils, F. Zerner[2] and D. Konstantinowsky[3] have published new evidence for the existence of subelectrons and it therefore becomes necessary to consider the nature of this new evidence. The new results are precisely like the old save in the two following particulars.

1. Great precaution is now taken to remove oxygen from the gas so as to prevent the possibility of the formation of oxides. Because of these precautions and because of the fact that certain droplets of mercury of ten or more times larger diameter than those used in his experiments are shown by microphotography to be spherical and to have metallic luster Professor Ehrenhaft assumes that *all of his ultra-microscopic* particles must also be spherical and uncontaminated.

Now in my judgment this evidence is wholly inconclusive and Professor Ehrenhaft has not yet touched the criticism that his irregularities must be looked for in a wrong assumption as to the shape, or the density, or the size, or the law of fall of his particles. Indeed I shall presently show that the evidence furnished by Professor Ehrenhaft's own data is very strongly in favor of such an explanation. Because some big mercury droplets, which he photographs, are spherical, is no indication that all particles are spherical, particularly particles a tenth or a hundredth as large as those which it is possible to photograph. Because he carefully frees his gas from oxygen, is no reason at all for thinking that when he strikes an electric arc between metals all kinds of combinations may not occur between the metal and the gases occluded in the electrodes. For that matter, in electric arcs I know from my own experiments that an inert gas like nitrogen becomes extraordinarily active in forming higher nitrogen compounds.[4]

The fact that these low values are found only with substances like mercury whose density would be greatly diminished by the addition of an oxide, or any other foreign substance, is a very suspicious circumstance, for if the density of the drop is smaller than the assumed density the apparent value of e will be too low. It is too low values of e which Professor Ehrenhaft always obtains whenever he obtains any irregularities at all.

[1] Wien Sitz. Ber., CXXIII., pp. 53–155, 1914. Ann. Phys., 44, p. 657, 1914.

[2] Phys. Zeit., 16, p. 10, 1915.

[3] Ann der Phy., 46, p. 261, 1915.

[4] Since this was written a paper has appeared by Strutt showing that active nitrogen thus formed attacks mercury. See Proc. Roy. Soc. 92, 438, '16; also 85, 219, '11.

2. The second new evidence presented is as follows: In 1911 Mr. Harvey Fletcher and the author first combined, in the Ryerson Laboratory, the observations of the up-and-down motion through a gas, under electrical and gravitational forces, of very minute droplets, with observations on the Brownian movements in the same gas of the same drops[1] when gravity was balanced by an electrical field. We were thus able to eliminate entirely the density of the drop and the resistance factor of the medium, and, provided only Einstein's Brownian movement equation

$$\overline{\Delta x^2} = \frac{2RT}{NK}\tau \tag{1}$$

is correct, to get with certainty the product Ne in the form

$$Ne = \frac{4RT(v_1 + v_2)_0}{\pi K F(\overline{\Delta x})^2}\tau. \tag{2}$$

This equation represents merely the elimination of the resistance factor K from the characteristic equation of the oil drop method, namely

$$\frac{v_1}{v_2} = \frac{mg}{Fe_n - mg} \quad \text{or} \quad e = \frac{mg}{Fv_1}(v_1 + v_2)_0 = \frac{K}{F}(v_1 + v_2)_0 \tag{3}$$

by means of (1) which may also be written,[2] in view of the Maxwell distribution law,

$$(\overline{\Delta x})^2 = \frac{4}{\pi}\frac{RT}{NK}\tau. \tag{4}$$

Now we found Ne to come out by this method the same as in electrolysis.[3] But Professor Ehrenhaft has in 1914 made what he regards as the same test on mercury particles and found Ne to come out in the case of 6 or 7 of the 9 particles on which he has published data[4] somewhat smaller than in electrolysis, though in 2 or 3 of the 9 drops it does not come out smaller. *These two points constitute the sum and substance of Ehrenhaft's addition since 1910 to the question in hand.* It is interesting to observe however, that Professor Ehrenhaft is at last in position to announce the important conclusion that electricity is atomic in structure because he too now finds a multiple relation between the charges carried by a single particle.

[1] Professor Ehrenhaft credits this advance to Weiss and ignores entirely the preceding work which appeared from this laboratory.

[2] PHYS. REV., I, 218, 1913.

[3] A brief summary of this work was given by the author in Science, Feb. 17, 1911, a more complete abstract by Mr. Fletcher in Phys. Zeit., 12, March, 1911, pp. 202–208, and in Le Radium, 8, pp. 279, July 1, 1911. See also Harvey Fletcher, PHYS. REV., 33, pp. 81, 1911, and R. A. Millikan, PHYS. REV., 1, pp. 218, 1913. On July 6, 1911, Dr. Edmund Weiss presented similar observations on silver particles before the Vienna academy, Vol. CXX., abt. II*a*, pp. 1020, and also found Ne to come the same as in electrolysis. He does not treat his data precisely in this way but assumes N from other determinations and then solves for e.

[4] See Wien Ber., CXXIII., pp. 52, 1914.

Now I wish first to point out certain general conditions which must be satisfied if reliable results are to be obtained, either by the Brownian movement method or by the law of fall method of determining e and to show why in my judgment Professor Ehrenhaft and his pupils obtain such results as they do, and second, I wish to consider what bearing their results, whatever their reliability, can have on the question of the existence of a subelectron.

6. The Brownian Movement Method and the Law of Fall Method of Determining e.

The Brownian movement method of determining e actually consists simply in determining Ne as described above and then inserting an *assumed* value of N and solving for e. Although it is possible to make the test of Ne in just the way described and although it was so made in the case of one or two of our drops, Mr. Fletcher worked out a more convenient method which involves expressing the displacements Δx in terms of fluctuations in the time required by the particle to fall a given distance, and thus dispenses with the necessity of balancing the drop at all. I shall present another derivation of this relation which is very simple and yet of unquestionable validity.

In equation (2) let τ be the time required by the particle, if there were no Brownian movements, to fall between a series of equally spaced cross-hairs whose distance apart is d. In view of such movements the particle will have moved up or down a distance Δx in the time τ. Let us suppose this distance to be up. Then the actual time of fall will be $\tau + \Delta t$ in which Δt is now the time it takes the particle to fall the distance Δx. If now Δt is small in comparison with τ, that is, if Δx is small in comparison with d (say 1/10 or less) then we shall introduce a negligible error (of the order 1/100 at the most) if we assume that $\Delta x = v_1 \Delta t$, in which v_1 is the mean velocity under gravity. Replacing then in (2) $(\overline{\Delta x})^2$ by $v_1^2(\overline{\Delta t})^2$ in which $(\overline{\Delta t})^2$ is the square of the average difference, without regard to sign, between an observed time of fall and the mean time of fall t_g, that is, the square of the average fluctuation in the time of fall through the distance d we obtain, after replacing the ideal time τ by the mean time t_g[1]

$$Ne = \frac{4}{\pi} \frac{RT(v_1 + v_2)_0 t_g}{F v_1^2 (\overline{\Delta t})^2} . \qquad (5)$$

In any actual work $(\overline{\Delta t})^2$ will be kept considerably less than 1/10 the mean time t_g if the irregularities due to the observer's errors are not to

[1] No error is introduced here if, as assumed, $\overline{\Delta t}$ is small in comparison with t_g. However, for more rigorous equations see Fletcher, PHYS. REV., 4, pp. 442, 1914; also Smoluchowski, Phys. Zeit., 16, p. 321, 1915.

mask the irregularities due to the Brownian movements so that (5) is sufficient for practically all working conditions. The work of Mr. Fletcher and of the author was done by both of the methods represented in equations 2 and 5. The difference is that in working with equation (2) one actually balances the drop, and then makes a long series of Δx measurements as in Brownian movement work in liquids. He then destroys the balance and, by producing changes in the number of electrons on the drop, takes a series of measurements of $(v_1 + v_2)$ using a large cross-hair distance and a constant field. The greatest common divisor of this series is the $(v_1 + v_2)_0$.

In working with equation (5) one does not balance the drop at all, but works out Ne from $(v_1 + v_2)_0$, taken just as before, and the square in the fluctuation $(\overline{\Delta t})^2$ in the times of fall between two cross-hairs between which the drops fall on the average in the time t_g. The first method involves simply the errors which are incidental to all Brownian movement work. It should yield reliable results if Δx is sufficiently large to be measured with some degree of certainty, and if enough displacements Δx have been taken to render the mean amenable to the law of averages. Hundreds or even thousands have usually been taken in all careful Brownian movement work. The method of equation (5), however, introduces the following two new errors which may be very large.

1. An observer's personal error in attempting to time a series of events happening at exactly equal time intervals will in general be one tenth or even two tenths of a second, depending somewhat on the observer. Now unless the fluctuations Δt due to this cause are *wholly negligible* in comparison with the mean fluctuation due to the Brownian movements in the time t_g, the observed $(\overline{\Delta t})$ in equation (5) will be too large and hence Ne too will come out too small.

2. If the drop is evaporating, or drifting out of the focal plane, or changing its speed regularly in any way while fluctuations due to Brownian movements are being taken, the changes in t_g due to this cause will be added to the Brownian movement fluctuations and will make the observed $(\overline{\Delta t})$ appear too large. It may even be several times larger than the value due to Brownian movements.

Finally it is altogether conceivable that if a body were of some shape other than spherical, for example spindle-shaped, it might always fall under gravity or rise in an electric field in such a way as to oppose a smaller surface to the resistance of the medium, than when it is knocking about irregularly under the influence of molecular bombardment. This cause too would make Ne come out too small. I have never found any evidence for such an effect as this, but the previously mentioned

sources of error are very real and very serious. In the case then of equation (5) all sources of error tend to make Ne come out too small.

When on the other hand we obtain e from the law of fall we use these two equations[1]

$$e_1 = \frac{4}{3}\pi\left(\frac{9\eta}{2}\right)^{\frac{3}{2}}\left(\frac{1}{g(\sigma - p)}\right)^{\frac{1}{2}}\frac{(v_1 + v_2)v_1^{\frac{1}{2}}}{F}, \tag{6}$$

$$e\left(1 + A\frac{l}{a}\right) = e_1. \tag{7}$$

The correction to Stokes's law represented by the last equation (7) makes the value of e_1 necessarily larger than e but, since this is always allowed for in all computations which are here under discussion, the only question which concerns us is as to how sources of error are likely to affect e_1 (6). The only uncertain element in this equation is the density of the particle, and when one is working with a dense metal like mercury or gold any surface contamination, or impurity of any sort, will tend to make the particle less dense than the assumed value and thus make e_1 appear too small. With a dust particle of loose structure e_1 might well come out a dozen times too small.

While then the Brownian movement method is independent of density, and probably not much dependent upon shape, the law of fall method is markedly dependent upon both of them, so that if both methods are rightly carried out a wrong assumption as to density or shape would make e by the law of fall method appear to come lower than the value found by the Brownian movement method. Now as a matter of fact all of the nine particles studied by Mr. Fletcher and myself in 1910 and 1911 and computed by Mr. Fletcher[2] showed the correct value of Ne while only six of them as computed by me fell on, or close to, the $e_1^{2/3}$, l/a, {or $e_1^{2/3}$, $1/pa$} line which pictures the law of fall of an oil drop through air.[3] (See also Fig. 1.) This last fact was not published in 1911 because it took me until 1913 to determine with certainty the complete law of fall of a droplet through air, in other words, to extend curves of the sort given in Fig. 1 to as large values of l/a as correspond to particles small enough to show large Brownian movements. As soon as I had done this I computed all of the nine drops which had given correct values of Ne and found that two of them fell far below the $e_1^{2/3}$, l/a, line, one more fell somewhat below, while one fell considerably above it. This meant obviously that these four particles were not spheres of oil alone, two of them falling much too slowly to be so constituted and one considerably too rapidly. There was nothing at all surprising about this result since I had explained

[1] PHYS. REV., XXXII, pp. 354, 378, 1911.

[2] Le Radium, 8, pp. 279, 1911; PHYS. REV., 33, pp. 107, 1911.

[3] PHYS. REV., 2, pp. 136, 1913.

fully in my first paper on oil drops[1] that until I had taken great precaution to obtain dust free air "the values of e_1 came out sometimes differently even for drops showing the same velocity under gravity." In the Brownian movement work no such precautions to obtain dust-free air had been taken because we wished to test the *general* validity of equations (2) and (5). That we actually used in this test two particles which had a mean density very much smaller than that of oil and one which was considerably too heavy was fortunate, since it indicated that our result was indeed independent of the material used.

It is worthy of remark that in general, even with oil drops, almost all of those behaving abnormally fall too slowly, that is they fall below the line of Fig. 1 and only rarely does one fall above it. This is because the dust particles which one is likely to observe, that is, those which remain long in suspension in the air, are either, in general, lighter than oil or else expose more surface than does an oil drop and hence act as though they were lighter. When one works with particles made of dense metals this behavior will be still more marked since all surface impurities of whatever sort will diminish the density. The possibility, however, of freeing oil-drop experiments from all such sources of error is shown by the fact that during the past year, although I have studied altogether as many as two or three hundred drops I do not recall that there has been a single one which did not fall within less than one per cent. of the line of Fig. 1.

7. EHRENHAFT'S AND ZERNER'S ANALYSIS OF OUR OIL DROP DATA.

Now, to return to the contention of Ehrenhaft and his pupils, they find, as stated above, first that in some instances Ne by the Brownian movement method comes out too small, and second that in general e comes out smaller by the law of fall method than by the Ne method and increasingly smaller the smaller the velocity of fall and hence the smaller the apparent size. So they contend that they have found subelectrons, but that these escaped my notice because I worked with so large droplets. *These extraordinarily minute charges of electricity can appear, so they assert, only on extraordinarily minute particles.*

Ehrenhaft and Zerner even analyze our reports on oil droplets and find that these also show in certain instances indications of subelectrons, for they yield, in these observers' hands, too low values of e whether computed from the Brownian movements or from the law of fall, and when the computations are made in the latter way e is found, according to them, to decrease with decreasing radius, as is the case in their experiments on mercury and gold particles.

[1] PHYS. REV., 33, pp. 366 and 367, 1911.

Now the single low value of *Ne* which they find in our work, is obtained by computing *Ne* from some twenty-five observations on the times of fall, and an equal number on the times of rise, of a particle which, before we had made any *Ne* computations at all, we reported upon[1] for the sake of showing that the Brownian movements would produce just such fluctuations as Ehrenhaft had observed when the conditions were those under which he worked.

Let us consider first this oil-drop evidence. Although it is obvious that in general very little significance can attach to attempts to test a statistical theorem on so few observations as we recorded in the case of this drop, yet it so happens that according to Mr. Fletcher's computation[2] of the data which he and I published in the Phys. Zeit., 12, pp. 162, 1911, on this drop Ne does come out from it within 2 per cent. of the correct value, namely 9,650 instead of 30 per cent. less as Ehrenhaft and Zerner find it to do. When, however, I compute *Ne* by equation (5) using merely the 25 times of fall, I find that the value of *Ne* comes out 26 per cent. low, which is about as Zerner finds it to do. If, however, I omit the first reading it comes out but 11 per cent. low. In other words the omission of one single reading changes the result by 15 per cent. and different groupings of the same observations make the 30 per cent. difference between Fletcher's and Zerner's results. This brings out clearly the futility of attempting to test a statistical theorem by so few observations as 25, *which is nevertheless more than Ehrenhaft usually uses on his drops.* Furthermore I have just shown that unless one observes under carefully chosen conditions his own errors of observation and the slow evaporation of the drop tend to make *Ne* obtained from equation (5) come out too low, and these errors may easily be enough to entirely vitiate the result. *There is then not the slightest indication in any work which we have thus far done on oil drops that Ne comes out too small.*

Next consider the apparent variation in *e* when it is computed from the law of fall. Zerner computes *e* from my law of fall in the case of the nine drops published by Fletcher, in which *Ne* came out the same as in electrolysis and finds, that one of them yields $e = 6.66 \times 10^{-10}$, one $e = 3.97 \times 10^{-10}$, one $e = 1.32 \times 10^{-10}$, one $e = 1.7 \times 10^{-10}$, while the other five yield about the right value, namely, 4.8×10^{-10}. In other words, as I had found before was the case (see above), five of these drops fall exactly on my curve (Fig. 1), one falls somewhat above it, one somewhat below, while two are entirely off and very much too low. These two, therefore, I concluded, were not oil at all but dust particles.

[1] Phys. Zeit., Vol. 12, pp. 162, 1911.

[2] Harvey Fletcher, Phys. Zeit., Sept., 1915.

Since Zerner computes the radius from the rate of fall, these two dust particles, which fall much too slowly, and therefore yield too low values of e must, of course, yield correspondingly low values of a. Since they are found to do so *Zerner concludes that our oil drops as well as Ehrenhaft's mercury particles yield decreasing values of e with decreasing radius.* His own tabulation does not show this. It merely shows three erratic values of e, two of which are very low and one rather high. But a glance at all the other data which I have published on oil drops shows the complete falsity of this position,[1] for this data shows that *after I had eliminated dust all of my particles yielded exactly the same value of e whatever their size.*[2] The only possible interpretation then which could be put on these two particles which yielded correct values of Ne but too slow rates of fall was that which I put upon them, namely, that they were not spheres of oil.

8. The Vienna Data on Mercury and Gold.

As to the Vienna data on mercury and gold, Ehrenhaft publishes, all told, data on just 16 particles and takes, for his Brownian movement calculations, on the average, only *15 times of fall and 15 times of rise on each, the smallest number being 6 and the largest 27.* He then computes by equation (5) his statistical average $(\overline{\Delta t})^2$, from such absurdly inadequate numbers of observations. Next he assumes Perrin's value of N, namely 70×10^{22}, which corresponds to $e = 4.1$, and obtains instead by the Brownian movement method, *i. e.*, the Ne method, the following values of e, the exponential term being for brevity omitted: 1.43, 2.13, 1.38, 3.04, 3.5, 6.92, 4.42, 3.28, .84. Barring the first three and the last of these the mean value of e is just about what it should be, as a matter of fact a little too high instead of too low, namely, 4.22 instead of 4.1. Further, the first three particles are the heaviest ones, the first one falling between his cross-hairs in 3.6 seconds and its fluctuations in time of fall are from 3.2 to 3.85 seconds, that is, only three tenths of a second on either side of the mean value. *Now these fluctuations are only slightly greater than those which the average observer will make in timing the passage of a uniformly moving body across equally spaced cross-hairs.* This means that in these observations, two nearly equally potent causes were operating to produce fluctuations. The observed Δts were, of course, then, larger than those due to Brownian movements alone, and might easily, with the few observations which were taken, be two or three times as large which would make Ne come out from four to nine

[1] PHYS. REV., II., pp. 138, 1913.

[2] See PHYS. REV., 2, pp. 134 and 135, 1913.

times too small. *It is only when the observer's mean error is wholly negligible in comparison with the Brownian movement fluctuations that this method will not yield too low values of e.* The overlooking of this fact is, in my judgment, the cause of some of the low values of *e* recorded by Ehrenhaft.

Again in the original work on mercury droplets, which I produced both by atomizing liquid mercury and by condensing the vapor from boiling mercury,[1] it was noticed that such droplets evaporated for a time even more rapidly than oil, and other observers who have since worked with mercury have reported the same behavior.[2] The amount of this effect may be judged from the fact that one particular droplet of mercury recently under observation in this laboratory had at first a speed under gravity of 1 cm. in 20 seconds, which changed in half an hour to 1 cm. in 56 seconds. The slow cessation, however, of this evaporation indicates that the drop slowly becomes coated with some sort of protecting film. Now if any evaporation whatever is going on while successive times of fall are being observed, the apparent $(\overline{\Delta t})^2$ may easily be several times as large as that due to Brownian movements even though these movements are large enough to prevent the observer from noticing, in taking twenty or thirty readings, that the drop is continually changing. One is disposed then from the established behavior of mercury drops to draw one or the other of two conclusions regarding Ehrenhaft's drops (1) either that they were not pure mercury or else (2) that his $(\overline{\Delta t})^2$ measurements were too large because of evaporation, and it is altogether conceivable that in the latter case they might be ten times too large. *There is, then, so far as I can see, no evidence at all in any of the data published to date by Ehrenhaft that the Brownian movement method actually does yield too low values of e.*

Konstantinowsky's data is very much like Ehrenhaft's in the possibility which it permits of too low values of *Ne* due to observational error and evaporation, but it emphasizes one further source of error which apparently leads the author entirely astray. He publishes *Ne* observations on just 11 particles,[3] five of which yield values of *e* between 3.3 and 4.2×10^{-10} or roughly correct values when the fact is considered that his chosen value of N is 70×10^{22}, three of the others yield about 2×10^{-10}, two more about 1×10^{-10}, while one yields $.5 \times 10^{-10}$. *His determination of the series of multiple relationships by which he gets the greatest common divisor* $(v_1 + v_2)_0$ *(see equation 6), is however so unreliable that he raises a question as to whether there is any greatest common divisor at all in spite of the fact that all other observers, a dozen of us now*

[1] PHYS. REV., 32, pp. 389, 1911.

[2] See Schidlof et Karpowicz, C. R., 158, pp. 1992.

[3] Ann. d. Phys., 46, pp. 292, 1915.

at least, including Ehrenhaft himself, now find these exact multiple relations invariably to hold. But an uncertainty in $(v_1 + v_2)_0$ (see equation 6) means an equal uncertainty in Ne. Konstantinowsky's very low values of Ne are then, in my judgment, due to the fact that he chooses the wrong value of $(v_1 + v_2)_0$. But with apparatus of his dimensions and particles as minute as he uses, it is not at all surprising that he cannot find the greatest common divisor of the series of speeds. *It would take more observations than he usually makes on a particle to locate it with certainty where the Brownian movements are as large as those which his particles ought to show, and where the field strengths are as small as those which he uses (nine volts only in some cases on condenser plates 2 mm. apart)* and hence where the drops are relatively heavily charged.

Let us next see why it is that Ehrenhaft's data show that, as we take smaller and smaller drops, the values of both a and e computed from the law of fall become farther and farther removed from the value of a and e computed from Brownian movements. To do this it is only necessary to consider how the density of the drop enters into the two methods.

The Brownian movement method, as used by him, consists first in solving equation (4) for K after inserting Perrin's value of N. (My K is his $1/B$ and to adapt (4) to his type of observation $(\overline{\Delta x})^2$ must be replaced by $v_1^2(\overline{\Delta t})^2$ and τ by t_g.) Knowing K correctly we can obtain m and e correctly from the equations which I experimentally verified in my first oil drop work, namely,

$$mg = Kv_1 \tag{8}$$

and

$$e = \frac{K}{F}(v_1 + v_2)_0. \tag{9}$$

So far no assumption has been needed as to the density and sphericity of the drop. If we wish to obtain a, however, we must get it from the assumption of a spherical drop, namely, from

$$m = \tfrac{4}{3}\pi a^3(\sigma - \rho)$$

which gives with (8)

$$a = \sqrt[3]{\frac{3}{4}\frac{Kv_1}{\pi(\sigma - \rho)g}}. \tag{10}$$

These equations show that any wrong assumption as to the density σ of the drop will not affect e, (9) but it will affect a, (10) a 9 per cent. error in $(\sigma - \rho)$ for example, appearing, in view of the cube root sign, only as a 3 per cent. error in a.

When now we compute e and a from the law of fall we see from equa-

tion (6) since e is proportional to $1/(\sigma - \rho)^{1/2}$ that a 9 per cent. error in $(\sigma - \rho)$ appears, in view here of the square root sign, as a $4\frac{1}{2}$ per cent. error in e. Again, from $mg = 6\pi\eta av$ or

$$\tfrac{4}{3}\pi a^3(\sigma - \rho)g = 6\pi\eta a v_1 \tag{11}$$

we see that

$$a = \sqrt{\frac{9}{2}\frac{\eta v_1}{(\sigma - \rho)g}}, \tag{12}$$

so that a 9 per cent. error in $\sigma - \rho$ involves also a $4\frac{1}{2}$ per cent. error in a. Suppose now there is a film of some foreign material which collects upon droplets of mercury thus making them a trifle lighter than pure mercury. This will not affect the e obtained from Brownian movements but it will make the e obtained from the resistance formula too small, since we have inserted too large a density in the denominator of equation (6). Again, this wrong assumption as to σ will affect a from (12) more than a from (10) the latter therefore appearing the larger. Further, the smaller the drop becomes the more will the two computations of e differ, the e from the law of fall becoming smaller and smaller with respect to the e from the Brownian movements. Similarly the a computed by the two methods will grow apart, the value obtained from the law of fall being influenced more by the wrong assumption as to density than the other. *Now this is precisely the behavior shown by all of Ehrenhaft's and Konstantinowsky's series of measurements on particles of mercury and gold.* All of these results follow in just the same way if the trouble is not with the density, but with the shape of the particles; for then the v_1 of equations (10) and (12) is too small, and hence the particle seems to be smaller than it is, but smaller from (12) than from (10).

If we then consider the Einstein Brownian movement equation established, there is only one possible conclusion to draw from Ehrenhaft's and Konstantinowsky's data, namely, that the few particles on which these authors publish observations have surface impurities, or nonspherical shapes, or else are not mercury at all. I have already commented on the illuminating fact that this data is all taken when they are working with the exceedingly dense substances, mercury and gold, and when, therefore, any thing not mercury but assumed to be, would yield very much too low values of e and a. The further fact that Ehrenhaft implies that normal values of e very frequently appear in their work[1] and that the low, erratic drops represent only a part of the data

[1] Wien Ber., CXXIII., pp. 59. "Die bei grösseren Partikeln unter gewissen Umständen bei gleicher Art der erzeugung haufig wiederkehrenden höheren Quanten waren dann etwa als stabilere raumliche Gleichgewichtsverteilungen dieser Sub-elecktron anzusehen, die sich unter gewissen Umstanden ergeben."

taken, is very suggestive. *When one considers too that in place of the beautiful consistency and duplicability shown in our oil drop work Ehrenhaft and his pupils never publish data on any two particles which yield the same value of e, but instead find only irregularities and erratic behavior*[1] just as they would expect to do with non-uniform particles, or with particles having dust specks attached to them, one wonders why any other explanation than the foreign material one, which explains all the difficulties, has ever been thought of. As a matter of fact in our work with mercury droplets at the Ryerson laboratory we have found that the initial rapid evaporation gradually ceases just as though the droplets had become coated with some foreign film which prevents further loss. Schidlof and Karpawicz find the same behavior of mercury drops and they further find that *this behavior as regards evaporation is the same in the purest nitrogen as it is in air.*[2] Ehrenhaft himself, in speaking of Brownian movements of his metal particles, comments on the fact that they seem at first to show large movements which grow smaller with time.[3] This is just what should happen if the radius is increased by the growth of a foreign film. In addition to all this we have very definite proof which will be presented later that mercury drops in the presence of oil vapor such as might come from stopcock grease do become coated with a film of oil.

Now what does Ehrenhaft say to these very obvious suggestions as to the cause of his troubles. Merely that he has avoided all oxygen and hence an oxide film is impossible and that he has photographed some big droplets and found them spherical. *Yet he makes his metal particles by striking an electric arc between metal electrodes, and the particles in question are not those which he photographs, for these are far below the limit of resolving power of any optical instrument.* In a word then Ehrenhaft's tests as to sphericity and purity are all quite worthless as applied to the particles in question, which according to him, have radii of the order 10^{-6} cm., a figure a hundred times smaller than the limit of sharp resolution.

[1] Their whole case is summarized in the tables in Ann. der Phys., 44, p. 693, 1914, and 46, p. 292, 1915, and it is recommended that all interested in this discussion take the time to glance at the data on these pages, for the data itself is so erratic as to render discussion of it needless.

[2] C. R., July, 1914.

[3] Phys. Zeit., 12, pp. 98. "Wie ich in meinen früheren Publikationen erwahnt habe zeigen die ultra mikroskopischen metall Partikel, unmittelbar nach der Erzeugung beobachtet eine viel lebhaftere Brownsche Bewegung als nach einer halben Stunde."

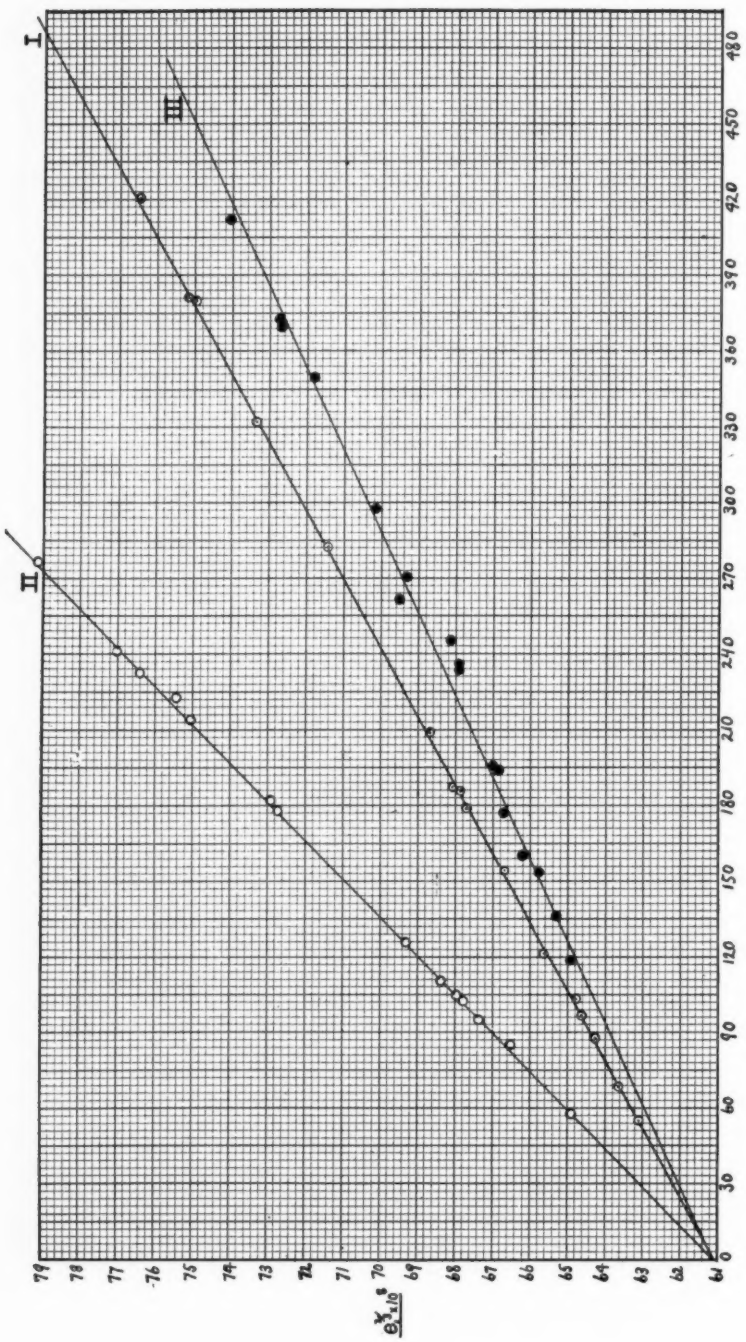

I
II
III
0
30
60
90
120
150
180
210
240
270
300
330
360
390
420
450
480
1/λα
79
78
77
76
75
74
73
72
71
70
69
68
67
66
65
64
63
62
61
X/e x 10^8

Fig. 1.

9. The Bearing of the Vienna Work on the Question of the Existence of a Subelectron.

But let us suppose that Ehrenhaft and Konstantinowsky do actually work with spherical particles of pure mercury and gold as they think they do, and that the observational and evaporational errors do not account for the low values of *Ne*, then what conclusion could be legitimately drawn from their data? Merely this and nothing more: (1) that Einstein's Brownian movement equation is not universally applicable, and (2) that the law of motion of their very minute charged particles through air is not yet fully known. So long as they find exact multiple relationships, as Ehrenhaft now does, between the charges carried by a given particle when its charge is changed by the capture of ions or by the direct loss of electrons, the charges on these ions must be the same as the ionic charges which I have accurately and consistently measured and found equal to 4.77×10^{-10} E.S. units. For they, in their experiments, capture exactly the same sort of ions, produced in exactly the same way as those which I capture and measure in my experiments. That these same ions have one sort of a charge when captured by a big drop and another sort when captured by a little drop is obviously absurd. If they are not the same ions which are caught in the two cases, then, *in order to reconcile the results with the existence of the exact multiple relationship found by Ehrenhaft as well as ourselves, it would be necessary to assume that there exist in the air an infinite number of different kinds of ionic charges corresponding to the infinite number of possible radii of drops, and that, when a powerful electric field drives all of these ions toward a given drop, this drop selects in each instance just the charge which corresponds to its particular radius.* Such an assumption is not only too grotesque for serious consideration but it is directly contradicted by my experiments, for I have repeatedly pointed out that with a given value of l/a I obtain exactly the same value of e_1 whether I work with big drops or with little ones.

10. New Proof of the Constancy of *e*.

For the sake of subjecting the constancy of e to the most searching test, I have recently made new measurements of the same kind as those heretofore reported, but using now a range of sizes which overlaps that in which Ehrenhaft works. I have also varied through wide limits the nature and density of both the gas and the drops. Fig. 1 (I.) contains new oil drop data taken in air; Fig. 1 (II.) similar data taken in hydrogen; Fig. 1 (III.) similar data on droplets of mercury in air. The radii of these drops, computed by the very exact method given in the PHYSICAL REVIEW (2), p. 117, 1913, vary tenfold, namely, from .000025 cm. to .00023 cm. Ehrenhaft's range is from .000008 cm. to

.000025 cm. It will be seen that these drops fall in every instance on the lines of Fig. 1 (I.) and (II.), and hence that they all yield exactly the same value of $e^{2/3}$, namely, 61.1×10^{-8}. The details of the measurements in air, which are just like those previously published, will be entirely omitted, but sample data on four of the drops in hydrogen are given in Tables I., II., III. and IV., and in Table V. is found a summary of the results on all the drops. The drop in Table I. will be seen to yield a value of $e^{2/3}$ which is a per cent. too high, because l/a is slightly above the limit at which I found the linear relation between $e_1^{2/3}$ and l/a to begin to break down[1] *but there is not a trace of an indication that the value of e becomes smaller as a decreases.* The coefficient of viscosity of hydrogen, namely $\eta_{23} = .0000884$, is in agreement with that obtained by multiplying the absolute value[2] of η for air at 23° C., namely, .0001824, by the value found by two recent observers Markowsky[3] and Gille[4] for the ratio between the viscosities of hydrogen and air. The

TABLE I.

Oil Drop in Hydrogen Falling 1.03 cm. in 8 Minutes.

t_g.	t_F.	n.	$\frac{1}{n}\left(\frac{1}{t_g}+\frac{1}{t_F}\right)$.	
	10.626	3	.03209	
	32.678			$V_i = 809.5$
	32.848			$V_f = 808.0$
	33.060			$t = 23.0°$ C.
				$p = 74.78$ cm.
460.0	15.830	2	.03262	$v_1 = .03249$
				$\eta_{23} = .00008841$
441.8	32.892			$a = .0000252$ cm.
471.8	33.192			$\frac{1}{pa} = 530.6$
455.4	33.802			
452.8	33.046			$\frac{l}{a} = 0.695$
442.4	32.740	1	.03166	
436.2	33.996			$e_1^{2/3} = 96.92$
445.0	33.104			
434.0	33.194			
448.8			.03170	$e^{2/3} = 61.9 \times 10^{-8}$

points on these two curves represent consecutive series of observations, not a single drop being omitted in the case of either the air or the hydrogen. This shows the complete uniformity and consistency which we

[1] PHYS. REV., 2, 138, 1913.

[2] Ann. der Phys., 1913.

[3] Ann. der Physik, p. 749, 1904.

[4] Ann. der Physik, Vol. 48, p. 825, 1916.

TABLE II.

Oil Drop in Hydrogen Falling 1.02 cm.

t_g.	t_F.	n.	$\frac{1}{n}\left(\frac{1}{t_g}+\frac{1}{t_F}\right)$.	
101.0	30.5			$V_i = 3252.8$
101.9	30.6	1		$V_f = 3244.5$
102.9	30.6			$t = 23.0°$ C.
				$p = 75.25$ cm.
103.4	13.6			$v_1 = .04303$
103.0	13.2	2	.04218	$\eta_{23} = .00008841$
				$a = .0000596$
103.1	30.5			$\frac{1}{pa} = 223.1$
103.1	30.8			
101.9	30.8	1	.04219	$\frac{l}{a} = .292$
102.7	30.1			
102.6	30.8			$e_1^{2/3} = 75.40 \times 10^{-8}$
102.6			.04219	$e^{2/3} = 60.9 \times 10^{-8}$

TABLE III.

Oil Drop in Hydrogen Falling 1.02 cm.

t_g.	$t_{F'}$.	n'.	$\frac{1}{n'}\left(\frac{1}{t_{F'}}-\frac{1}{t_{F''}}\right)$.	n.	$\frac{1}{n}\left(\frac{1}{t_g}+\frac{1}{t_F}\right)$.	
18.638	42.122					
18.720	42.466					
18.616	41.916					
18.505	41.519			6	.01292	
18.656	42.070					
18.579	41.780					$V_i = 2456.2$
18.596	41.922					$V_f = 2452.6$
		1	.01283			$t = 22.88°$ C.
18.588	91.712					$p = 39.40$
18.588	93.012					$v_1 = 0.01313$
18.569	93.228			5	.01289	$\eta = 0.00008841$
18.692	95.416					$a = 0.000143$
18.648	94.628					$\frac{1}{pa} = 178.1$
		1	.01275			
18.497	42.828					$\frac{l}{a} = 0.233$
18.459	43.016					
18.376	43.141					$e_1^{2/3} = 72.71 \times 10^{-8}$
18.586	43.190			6	.01282	
18.514	43.200					
18.456	42.926					
		1	.01310	5	.01276	
18.426	98.590					
18.472	99.246					
18.560			.01289		.01287	$e^{2/3} = 61.11 \times 10^{-8}$

TABLE IV.

Oil Drop in Hydrogen Falling 1.02 cm.

t_g.	t_F.	n'.	$\frac{1}{n'}\left(\frac{1}{t_F}-\frac{1}{t'_F}\right)$	n.	$\frac{1}{n}\left(\frac{1}{t_g}+\frac{1}{t_F}\right)$.	
7.726	65.146					
7.742	64.102					
7.632	63.240					
7.742	62.624			13	.01112	
7.728	61.782					
7.760	61.308					
7.750	61.394					
		1	.01132			
7.808	36.176					
7.742	35.822			14	.01118	
7.838	35.754					
		1	.01109			$V_i = 3928.0$
7.778	59.340					$V_f = 3920.6$
7.750	59.320			13	.01119	$t = 23.02°$ C.
		3	.01114			$p = 74.27$ cm.
7.734	19.926					$v_1 = 0.011434$
7.828	19.566					$\eta = 0.00008841$
7.716	19.732			16	.01121	$a = 0.000233$
7.734	19.600					$\frac{1}{pa} = 57.7$
		3	.01113			
7.774	57.900					$\frac{l}{a} = 0.0756$
7.810	57.296			13	.01123	
7.856	57.354					$e_1^{2/3} = 64.89 \times 10^{-8}$
		1	.01128			
7.848	34.880			14	.01124	
7.816	34.708					
		5	.01119			
7.846	11.784					
7.738	11.836			19	.01122	
7.732	11.774					
		6	.01119			
7.780	57.120					
7.814	56.632					
7.754	57.340			13	.01124	
7.794	57.186					
7.769			.01119		.01121	$e^{2/3} = 61.10 \times 10^{-8}$

have succeeded in obtaining in the work with oil drops. That mercury drops show a similar behavior was somewhat imperfectly shown in the original observations which I published on mercury.[1] I have since fully confirmed the conclusions there reached. That mercury drops can with suitable precautions be made to behave practically as consistently as oil is shown in Fig. 1, III, which represents data obtained by blowing into

[1] PHYS. REV., pp. 389–390, 1911.

TABLE V.

No.	$t°$ C.	p Cm. Hg.	PD Volts.	t_g Sec.	n.	$a \times 10^5$ Cm.	$\frac{1}{pa}$	$e_1^{2/3} \times 10^8$.	$e^{2/3} \times 10^8$.
1	23.0	74.78	808.5	44.88	1–3	2.52	530.5	96.92	61.9
2	23.0	19.05	1,644.2	17.05	7–11	13.64	385.0	86.46	61.22
3	23.0	30.99	1,638.8	34.78	3–4	9.74	331.4	83.05	61.00
4	23.0	40.64	2,445.0	53.23	1–2	7.94	309.8	81.65	60.92
5	23.0	30.74	1,639.5	25.03	5–12	11.76	276.6	79.14	61.24
6	23.0	30.46	1,640.3	19.20	7–8	13.65	240.5	77.04	61.06
7	23.0	40.57	2,460.5	32.56	2–3	10.59	232.6	76.39	61.01
8	23.0	75.40	3,248.5	10.26	1–2	5.96	223.1	75.40	60.9
9	23.0	40.41	2,448.8	27.47	3–8	11.55	214.2	75.02	60.90
10	23.0	40.19	2,451.0	20.16	5–8	13.67	182.0	72.88	61.27
11	22.9	39.40	2,454.4	18.61	5–6	14.25	178.1	72.71	61.12
12	23.0	73.59	3,280.0	33.56	2–3	10.78	126.0	69.31	61.26
13	23.0	74.78	3,266.5	27.58	2–5	12.07	110.7	68.36	61.08
14	23.0	74.46	3,915.5	24.55	2–5	12.84	104.6	67.94	61.06
15	22.9	74.40	3,288.0	23.63	3–6	13.12	102.4	67.74	61.00
16	23.0	73.31	3,287.8	19.76	4–7	14.37	94.9	67.36	61.02
17	23.0	75.88	3,278.1	17.54	5–8	15.34	85.8	66.56	60.88
18	23.0	74.27	3,924.3	7.78	12–19	23.34	57.7	64.89	61.11
								Mean.	61.11

the observing chamber above the pinhole in the upper plate a cloud of mercury droplets formed by the condensation of the vapor arising from boiling mercury. This data has just been taken in the Ryerson Laboratory with my apparatus by Mr. and Mrs. John B. Derieux. Since the pressure was here always atmospheric, the drops progress in the order of size from left to right, the largest having a diameter about three times that of the smallest, the radius of which will be seen from Table V. to have been .00003244 cm. It will be seen that a way has here been found to largely eliminate the evaporation of the mercury drops, so marked in most preceding work of this kind on mercury.

It is not claimed that this work constitutes a determination of e which compares in precision with that attained in the oil drop work previously published, but it does show that the line through the point $e^{2/3} = 61.1 \times 10^{-8}$ lies very close to all the points observed and hence that my original determination of e at 4.774×10^{-10} cannot be much in error.

A glance at the value of $e^{2/3}$ in the lower right hand corner of each of these tables is enough to establish with absolute conclusiveness the correctness of the assertation that the apparent value of the electron is not in general a function of the radius of the drop on which it is caught, even when that drop is of mercury, and even when it is as small as some of those with which Ehrenhaft obtained his erratic results. If it appears to be so with his drops, the cause cannot possibly be found in actual fluctuations in the charge

TABLE V.

Mercury Drop No. 1 Falling 1 cm. in Air.[1]

t_g.	t_F.	n'.	$\frac{1}{n'}\left(\frac{1}{t_{F'}}+\frac{1}{t_F}\right)$.	n.	$\frac{1}{n}\left(\frac{1}{t_g}+\frac{1}{t_F}\right)$.	
39.89	8.13					
39.91	8.03					
39.82	7.90			4	.0376	
39.79	7.91					
		1	.0372			
	11.28					
	11.30					
	11.54			3	.0377	
	11.51					
	11.22					
		1	.0380			$V_i = 3935$
	20.16					$V_t = 3875$
	0.12					$t = 23.05$
	19.95			2	.0373	$p = 75.98$
	20.05					$v_1 = .02464$
	19.95					$\eta = .0001824$
		1	.0372			$a = .0000362$
	78.4					
	79.2			1	.0373	$\frac{1}{pa} = 369.4$
	78.0					
		1	.0380			$\frac{l}{a} = .2666$
	19.81					$e_1^{2/3} = 72.63 \times 10^{-8}$
	19.61					
	19.79			2	.0374	
	19.75					
	19.69					
41.41		1	.0382			
41.21	11.19					
41.38	11.30					
41.20	11.31			3	.0377	
41.21	11.25					
41.46	11.26					
40.58			.0377		.0375	$e^{2/3} = 61.3 \times 10^{-8}$

of the electron without denying completely the validity of my results. But these results have now been checked in their essential aspects by scores of observers, including Professor Ehrenhaft himself. Furthermore, my results are not the only ones with which Ehrenhaft's contention clashes; it is at variance also with all experiments like those of Rutherford and Geiger and Regener on the measurement of the charges carried by α and β particles, for these are infinitely smaller than any particles used by Ehrenhaft and if, as he contends, the value of the unit out of which a charge is built up is smaller and smaller the smaller the capacity of the body on which it is found, then these alpha-particle charges ought

TABLE VI.

Mercury Drop No. 3 Falling 1 cm. in Air.

t_g.	t_F.	n'.	$\frac{1}{n'}\left(\frac{1}{t_F}-\frac{1}{t_F}\right)$.	n.	$\frac{1}{n}\left(\frac{1}{t_g}+\frac{1}{t_F}\right)$.	
48.09	50.8					$V_i = 3800$
47.48	50.4					$V_i = 3745$
47.97	50.9			1	.0405	$t = 22.90$
47.89	50.1					$p = 74.84$
47.71		1	.0409			$v_1 = .02082$
48.48	16.50					$\eta_{23} = .0001824$
48.64	16.52			2	.0407	$a = .00003244$
						$\frac{1}{pa} = 411.8$
						$\frac{l}{a} = .2928$
						$e_1^{2/3} = 74.05 \times 10^{-8}$
47.92			.0409		.0406	$e^{2/3} = 61.3 \times 10^{-8}$

to be extraordinarily minute in comparison with the charges upon our oil drops. Instead of this, the charge on the alpha-particle comes out nearly twice the charge which I measure in my oil-drop experiments.

While then it would not be in keeping either with the spirit or with the method of modern science to make any dogmatic assertion about the existence or non-existence of a subelectron it can be asserted with entire confidence that there is not in Ehrenhaft's experiments a scrap of evidence for the existence of charges smaller than the electron. If all of his assumptions as to the nature of his particles are correct then his experiments mean simply that Einstein's Brownian movement equation is not of universal validity and that the law of motion of minute charged particles is quite different from that which he has assumed. It is very unlikely that either of these results can be drawn from his experiments for Nordlund[1] and Westgren[2] have apparently verified the Einstein equation in liquids with very much smaller particles than Ehrenhaft uses and on the other hand, while I have worked with particles as small as 2×10^{-5} cm. and with values of l/a as large as 100, which is very much larger than any which appear in the work of Ehrenhaft and his pupils, I have thus far found no evidence of a law of motion essentially different from that which I published in 1913.

[1] Zeitschr. für Phys. Chem., 87, 40, 1914.

[2] Untersuchungen über Die Brownsche Bewegung u. s. w. Inaugural Dissertation von Arne Westgren, Uppsala & Stockholm, 1915.

TABLE VII.

Mercury Drop No. 2 Falling 1 cm. in Air.

t_g	t_F	n'.	$\frac{1}{n'}\left(\frac{1}{t_{F'}}-\frac{1}{t_F}\right)$.	n.	$\frac{1}{n}\left(\frac{1}{t_g}+\frac{1}{t_E}\right)$.	
9.92	6.00					
9.83	5.90					
9.85	5.80			14	.0194	
	5.94					
		4	.0197			
	11.02					
	10.92					
9.76	10.97					
	11.01					
	10.98			10	.0193	
	11.04					
	10.94					
9.76	11.01					
	11.15					
		1	.0195			
	14.05					
	13.96			9	.0193	
9.66	14.06					V_i = 4685 volts
		4	.0194			V_f = 4615 volts
	6.68					t = 23° C.
	6.67			13	.0193	p = 74.61 cm.
9.67	6.79					v_1 = .1024 cm./sec.
	6.75					η = .0001824
		4	.0193			a = .00007575
	14.07					$\frac{1}{pa}$ = 177.4
	13.93					
9.72	13.92			9	.0193	$\frac{l}{a}$ = .1253
	13.98					
		1	.0199			$e_1^{2/3} = 66.75 \times 10^{-8}$.
	19.26					
	19.29			8	.0193	
9.55	19.39					
	19.52					
		2	.0194			
	76.8					
	77.4			6	.0192	
	77.3					
	77.8					
		1	.0188			
	31.54					
	31.36			7	.0191	
9.82	31.47					
	31.84					
		1	.0192			
	19.7			8	.0192	
	19.6					
9.72	19.51					

t_g	t_F	n'.	$\frac{1}{n'}\left(\frac{1}{t_{F'}}-\frac{1}{t_F}\right)$.	n.	$\frac{1}{n}\left(\frac{1}{t_g}+\frac{1}{t_F}\right)$.	
9.72	19.67	2	.0192			
	8.0					
	8.0			6	.0192	
	7.92					
9.79	7.90	1	.0187			
9.97	3.17			7	.0191	
9.79	3.23					
9.77			.01932		.01925	$e^2/s = 61.1 \times 10^{-8}$

11. SUMMARY.

In conclusion then:

1. Professor Ehrenhaft has published no adequate test of whether *Ne* by the Einstein Brownian movement method comes out for his particles the same as in electrolysis. I have tested it very roughly for Hg particles of size about $a = 2.5 \times 10^{-5}$ and Fletcher and Eyring have tested it very accurately for oil particles of this size and found it to hold. It will probably hold for Ehrenhaft's particles when given a reliable test.

2. If it should not be found to hold his result will have no bearing whatever upon the question of the existence of a subelectron. It will mean merely that the Einstein equation is not applicable in gases to charged particles of all sizes.

3. All of Professor Ehrenhaft's results are easily explained on the assumption of incorrect assumptions as to the density and sphericity of his particles, but even if these assumptions are correct, yet his results have no bearing on the question of the existence of a subelectron. They mean simply that he has assumed an incorrect law of movement of his minute charged particles through a gas.

4. The non-appearance of a subelectron in Professor Ehrenhaft's experiments is demonstrated by the existence of a multiple relationship between the charges carried by a given particle taken in conjunction with my direct proof extended in this paper that the apparent value of e is not in general even with mercury droplets a function of the radius of the drop on which it is found. The opposite assumption invoked by Professor Ehrenhaft not only involves a grotesque assumption as to the nature of ionization but is flatly contradicted by my experiments.

5. There has appeared up to the present time, I think, no evidence whatever for the existence of a subelectron.

I have to thank Mr. Wm. Gaertner for the loan of the magnificent printing chronograph with which the above time determinations have been made, and Dr. Yoshin Ishida for able assistance in the experimental work as well as in computing the observations.

THE ELECTRICAL CONDUCTIVITY OF A BUNSEN FLAME FOR SMALL DISTANCES BETWEEN THE ELECTRODES.

BY NORMAN HURD RICKER, B.A.

IF two platinum discs are immersed in a flame, and a potential difference maintained between them, a current will flow through the flame, and it can easily be measured by means of a galvanometer. The usual method of measuring the conductivity of a flame has been to employ a very long flame, consisting of a row of small burners side by side, and two platinum disc electrodes which can be moved about in the flame. It has been found[1] that there is a uniform potential gradient in the part of the flame from the anode close up to the cathode, while close to the cathode there is a large fall of potential. The relation, found by H. A. Wilson, between the current through the flame, the distance between the electrodes, and the potential difference, is given by

$$V = ACd + BC^2 \tag{1}$$

where V represents the potential difference; C, the current; d, the distance between the electrodes; and A and B are constants. The term ACd is due to that part of the flame in which there is a uniform potential gradient, and the term BC^2 to the fall of potential near the cathode. According to this formula, which is derived experimentally[1] when d is large, and theoretically[2] on the assumption that the current is far from saturation, C should be independent of d when d is small, V being kept constant. However with the above mentioned apparatus, any departure from this formula when the electrodes are brought close together, would be masked by the current around the backs of the electrodes, which would give a value of the distance much larger than the real distance between the electrodes. The object of the following work was, therefore, to eliminate this conduction around the backs of the electrodes and thereby get the true distance effect, and to see if there is any departure from the above formula when d is small.

APPARATUS AND METHOD.

The arrangement of the apparatus used in the experiments is shown in Fig. 1. The air, kept at a constant pressure, as shown, and the gas,

[1] H. A. Wilson, Phil. Mag., Oct., 1905, p. 476.

[2] J. J. Thomson, "Conduction of Electricity through Gases," 1906, p. 92.

with a manometer in its inlet tube, were fed into a mixing chamber *m.c.*, and then to the burner. The gas used was gasoline vapor. This gave a steady, hot, flame, which kept the electrodes, *e*, at a yellow to white heat. A brass cylinder was placed about the lower part of the flame to steady it. The electrodes, of which there were three, were connected as shown in the diagram. The outer electrodes were connected together, and could be moved together and apart by means of a micrometer screw of 1 mm. pitch, with its head divided into 100 parts (Fig. 2).

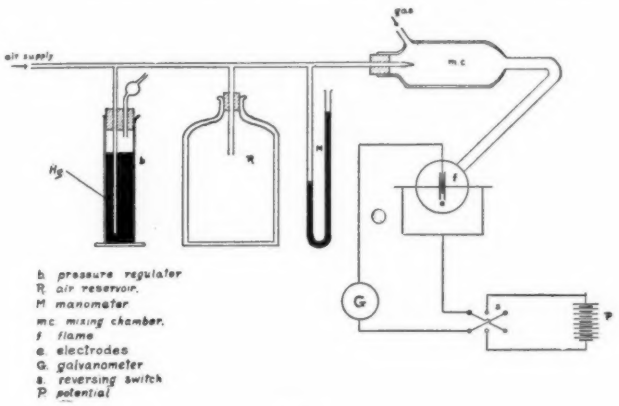


Fig. 1.

One electrode was fastened to a block worked by a right-hand screw, and the other to a block worked by a left-hand screw, both screws being cut on the same shaft. The central electrode was a disc about 10 mm. in diameter, cut from sheet platinum, with a strip projecting out of the flame for support. This electrode, which was the cathode in all of the experiments, was kept fixed, and the outer electrodes moved up to it. The discs were carefully paralleled, and so it was possible to work at very small distances.

During the preliminary experiments it was found that, unless the electrodes were scrupulously clean, the galvanometer would rush to a very high value when the circuit was closed, and gradually drift back. It would take about twenty minutes to reach a steady value. The decay of the current with the time was apparently exponential. When the current was stopped and again started, the galvanometer rushed off as before, again drifting back. Therefore, in order to clean the electrodes thoroughly, they were boiled in HCl for several hours, and then heated in the flame for a considerable time before beginning any experiments. After this treatment it was found that, upon closing the circuit, the current went immediately to a steady value.

The use of the compressed air supply was found necessary, for, in the preliminary experiments, with an ordinary burner with exterior air inlet, salt puffs from the dust in the air were rapidly admitted to the flame, keeping the galvanometer constantly jumping about. The potential was furnished by a battery of small dry cells giving about 150 volts per 100. These are shown at *P*. In order to measure the distance between the electrodes, the reading of the micrometer was taken at an unknown distance, and the micrometer then moved until the electrodes touched, as indicated by the galvanometer flying off the scale. The micrometer was again read — the difference giving the distance between the electrodes. Protective resistances of $CuSO_4$ in glycerine were provided for the galvanometer. As a check on the constancy of the flame, before beginning any set of readings, the electrodes were set at a certain standard distance apart and a standard potential applied. The resultant current was never found to vary more than 5 per cent.

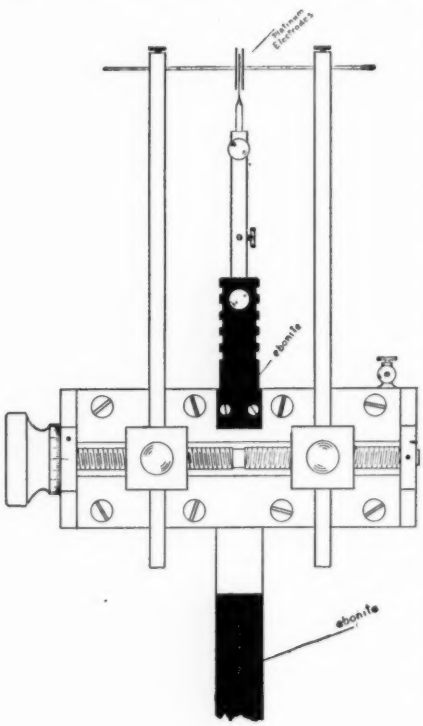


Fig. 2.

RESULTS.

The variation of the current through the flame with the distance between the electrodes was first observed—the potential being kept constant. It was found at distances less than 1 cm., that, as the distance was decreased, the current decreased, reached a minimum at about .6 mm., and, as the distance was further decreased, rose rapidly to a high value. This was observed for a number of values of the potential difference, from 1.5 volts up to 300 volts. Typical curves, showing this variation of the current with the distance between the electrodes, are shown in Fig. 3.

If the formula $V = ACd + BC^2$ held for all values of d, then for small values of d, the curve should be as represented by the dotted line, Fig. 5. This equation, as before stated, is derived on the assumption that the

current is far from saturation. As the distance becomes smaller, however, the number of ions between the electrodes becomes smaller, and there is then more likelihood of saturation. If the current should reach

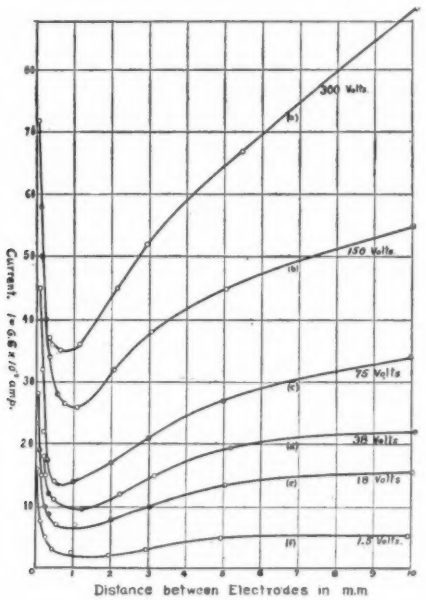


Fig. 3.

a saturation value, then a decrease in d would produce a decrease in C. To see if the current had really become saturated when the electrodes were close together, the electrodes were fixed at about .2 mm. apart, and the variation of C with V observed. The relation is shown in Fig. 4. It appears from this curve that the current has apparently about become saturated when the potential is above about 15 volts. For distances greater than 0.5 cm. the curves showing the variation of C with V were found to be approximately parabolas, showing that at these distances the above formula was beginning to hold. It is then fair to suppose that this decrease in C, as d in decreased, is due to a decrease in the number of ions between the electrodes. But why should the current reach a minimum and then rise again? The first explanation that suggested itself was that ionization by collision had begun to take place; but this idea soon failed, for the variation of C with V at very small distances gave a curve similar to Fig. 4, while if ionization by collision had begun to take place, it would be expected that the curve should rise again. Moreover, the rise in C, as d approached zero, was obtained with potentials as small as 1.5 volts, which is too small to produce ionization by collision. The

ionization by collision theory was then discarded, and the effect explained as follows.

It is well known that when a body is raised to incandescence, ions are emitted from its surface. The currents carried by these ions may be made fairly large when the incandescent body is placed in a vacuum, but

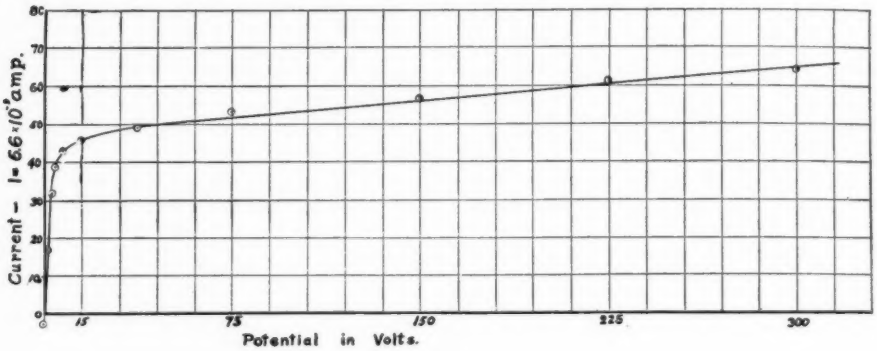


Fig. 4.

when a gas is present, the motion of the ions is retarded and some of them diffuse back to the incandescent electrode.

Let I be the maximum possible thermionic current from the hot electrode, and i the actual current observed. Now assuming that when an ion strikes the electrode it gives up its charge, and that the current

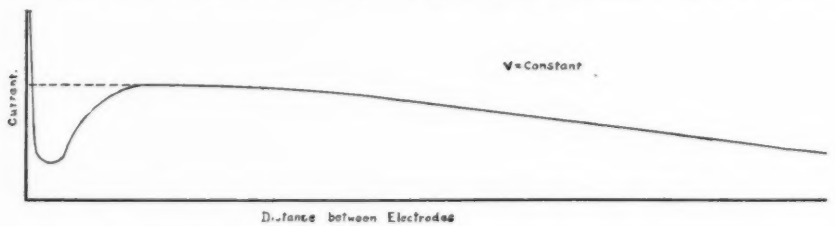


Fig. 5.

due to volume ionization in the gas is so small as to be negligible, $(I - i)$ will represent the charge carried back per second by diffusion. If there are n ions per cc. close to the electrode, then on the kinetic theory of gases, the number of ions striking it per sq. cm. per sec. is

$$\frac{nu}{\sqrt{6\pi}},$$

where u is the velocity of agitation of the ions. We then have,

$$I - i = \frac{nue}{\sqrt{6\pi}}.$$

Since $i = kneX$ and $k = 1.4\, e\lambda/mu$, where X is the field intensity; λ, the mean free path, and m, the mass of the ion, the equation becomes,

$$i = \frac{IX}{X + \frac{mu^2}{1.4\, e\lambda/6\pi}}$$ [1]

Since mu^2/λ is independent of the temperature, we can replace it with a constant, so that $i = IX/(X + B)$, where B is a constant.

Now if we assume that, for small values of d, the field is uniform, we have

$$\frac{V}{d} = X,$$

so that

$$i = \frac{IV}{V + Bd}$$

or

$$i = \frac{I}{1 + Bd/V}.$$

This equation is that of a rectangular hyperbola shifted slightly to the left along the d axis. However we have neglected the volume ionization due to the gas. This is proportional to the distance between the electrodes as long as the current is saturated, so that

$$i = \frac{I}{1 + Bd/V} + Cd, \tag{3}$$

where C is a constant, and the term Cd represents the current due to volume ionization.

These curves (Equation 3) have minima and are very similar to the experimental curves for small values of d. However, as d becomes large, the current is no longer saturated, and the curve bends over instead of approaching the line, $i = Cd$, asymptotically. That is to say C is not a constant except when d is small.

The actual values of the current when d was less than about .2 mm. could not be relied upon for calculations, because of the magnified effect of small irregularities of the surfaces of the electrodes. The determination of I was therefore not attempted.

SUMMARY.

The variation of the current through the flame with the distance between the electrodes was investigated, and found to be as shown in Fig.

[1] H. A. Wilson, "The Electrical Properties of Flames and of Incandescent Solids," p. 40. J. J. Thomson, "Conduction of Electricity through Gases," 1906, p. 208.

3. As d is diminished, the decrease in the current was shown to be due to the current becoming saturated, and the volume decrease causing a decrease in the current. The curve reaches a minimum and then rises again. This rise is explained by the intense field increasing the thermionic current, and was shown not to be due to ionization by collision. The relation between the current and the distance between the electrodes for all values of d is shown in Fig. 5.

In conclusion I wish to express my most sincere thanks to Prof. H. A. Wilson, F.R.S., for his kindly interest in these experiments, and for his valuable advice during the investigation.

PHYSICAL LABORATORY,
THE RICE INSTITUTE,
HOUSTON, TEXAS.

ON THE MOBILITIES OF GAS IONS IN HIGH ELECTRIC FIELDS.

BY LEONARD B. LOEB.

I.

INTRODUCTION AND STATEMENT OF PROBLEM.

THE earliest experiments on the diffusion of the ordinary gaseous ion revealed the fact that the diffusion coefficients of the ions into a gas were about a tenth as great as the diffusion coefficients of similar uncharged molecules into the same gas. This low diffusion coefficient also manifests itself in the comparatively low order of magnitude of the values of the mobilities of the gaseous ions (*i. e.*, the comparatively low velocities of the ions in unit electric field). An attempted explanation of this was made as early as 1897[23] through the assumption that the ions were not single charged molecules, but rather groups of molecules clustered around an electron or a positive atomion. One of the early mathematical derivations of the "cluster" theory was due to Langevin[1] and estimated that the cluster consisted of about ten molecules. An attempt was made in 1909 by Wellisch,[2] and also by Sutherland,[3] to account for the low mobilities of the ions by assuming that they consisted of single charged molecules. The lowering of the mobility coefficients was on this view ascribed to a retardation of the ion in its path through the gas in virtue of its charge. The charge on the ion would cause it to exert attractive forces on the uncharged gas molecules. Thus the ion in traversing unit distance through the gas would encounter more collisions with the gas molecules than would an uncharged molecule. The retardation of this "small ion" in its path through the gas due to the charge would be equivalent to that caused by the increase in the size of the ion assumed by the "cluster" theory. Both the "cluster" and the "small ion" theories explain a number of phenomena exhibited by the ions about equally well. There are however radical differences between the consequences of the two theories which should, if investigated experimentally, lead to the adoption of one to the exclusion of the other.

On the assumption of a "cluster" ion we should expect, under circumstances where the cluster acquires a high kinetic energy, that it might suffer disintegration upon impact. Such a disintegration, or

breaking up of ions, would obviously manifest itself by an abnormal increase of the mobility. The kinetic energy might be gained by the ion if it fell through a sufficiently high potential difference in traversing a mean free path. The value of the kinetic energy at which the disintegration should occur would depend on the potential energy of the ion cluster. The breaking up, or the abnormal increase in mobility of the ion cluster, should take place at approximately the same value of field strength times mean free path for both the positive and the negative ion clusters.

The "small ion" theory would naturally not lead one to expect any such result. The mobility of the ions should remain approximately constant with possibly only slight variations in its value until fields were reached near which ionization by collision could take place. In fields of such strength it is conceivable that the negative ion might acquire sufficient energy to knock off its electron. The positive ion would undergo no such change, retaining an approximately constant mobility.

This predicted difference in the behavior of the positive ion, from the standpoint of the two theories, would enable one to distinguish definitely between them, were the actual behavior of the positive ion known. If the positive ion were conclusively shown to acquire an abnormally high mobility in fields in which it would experience high values of the product of field strength times the mean free path, the "cluster" theory would be established. The proof, however, would not be so certain, were such an abnormality discovered in the case of the negative ion: For this abnormality might be interpreted in the light of the "small ion" theory as being due to the fact that under certain circumstances the highly mobile negative electron existed in a free state, *i. e.*, unattached to a molecule. Consequently experiments which could lead to a determination of the mobility of the positive ion under such circumstances are absolutely necessary to distinguish between these two theories.

Attempts in this general direction were made by numerous observers (Kovarick,[4] Lattey,[5] Todd,[6, 7] Townsend[8]). For reasons which will become obvious later, most of their work was done by allowing the ions to acquire kinetic energy by falling through long mean free paths at comparatively low potentials. In other words, these experimenters worked with small electric fields, at low gas pressures. The positive ions showed abnormal mobilities only in the results of Todd,[6, 7] who worked at extremely low pressures. To the writer's knowledge it is only in the study of the discharge of electricity from points that an attempt has been made to estimate the mobilities of the ions under

conditions in which they were subjected to high fields at high pressures. Chattock,[9] in fields estimated as high as 3,000 volts per cm., found perfectly normal values of the mobility for both ions by this method. Franck,[10, 18] Moore,[22] and others, using this method in fields of about 10,000 volts per cm., found the mobilities of both ions to be abnormally high. Not much confidence should be placed on these results as a means of differentiation between the two theories, for the results of the various observers do not agree. Furthermore, the field strength at which these mobilities were determined can merely be guessed at, for the nature of the field is absolutely unknown.

Since no work has been done in this field before, and since it offered possibilities of investigating the mobilities of the positive and negative ions under conditions which might lead to a differentiation between the two theories, it was considered of interest to determine the mobilities under high electric fields at higher pressures. Accordingly, at the suggestion of Professor Millikan, this problem was undertaken by the writer.

II.

MODES OF ATTACK ATTEMPTED IN THIS WORK.

The method of measurement decided upon as being the most suitable for these purposes was the Franck[10, 19] modification of the Rutherford[17] alternating current method. Even with this comparatively simple method the problem becomes one of considerable technical difficulty. Since the velocity of the ion varies directly with the field strength, the velocity of the ion will be high. In order to be able to catch the ions between the gauze and the plate when the distance between them is small enough so that the field between them is approximately uniform, the period over which the accelerating field acts on the ions must be very short. In other words, the frequency of the alternations must be very high. The problem is then to obtain an alternating potential difference whose value is high, and whose frequency of alternation is great enough to enable small plate distances to be used. The difficulties of this task were the chief factor which limited the determinations of the other observers to low fields and low pressures.

The first attempt was made to obtain such an alternating potential difference by means of a commutator scheme. For this purpose a commutator was built of ebonite 25.5 cm. in diameter with 20 brass segments, 2.6 cm. long. It was fastened to the shaft of a well balanced motor which was capable of giving a speed of 2,200 revolutions per minute. The potential difference was obtained from a bank of small lead storage cells. Work with this apparatus was carried on for about four months

in the winter of 1914. Field strengths up to 1,000 volts per cm. were worked with. With the maximum frequency of alternation obtainable, these fields of 1,000 volts per cm. formed the upper limit of fields that could be handled with any degree of certainty. Furthermore, at the potential difference of 2,000 volts which were necessary to give these field strengths, serious sparking around the commutator occurred. This sparking finally became so bad that the brushes used burnt out several times during a three-hour determination, and this commutator was discarded. The results indicated no marked increase in the mobility of either ion. As this was near the limit of frequency of alternation which could be obtained at these potentials by any commutator scheme obtainable at the Ryerson laboratory, the commutator method was abandoned.

Through the courtesy of Director Stratton of the Bureau of Standards, for which the writer wishes to express his gratitude, an attempt was made during the summer of 1913 to utilize the high frequency sine wave generator belonging to the Bureau. The generator has a range of frequencies extending from 10,000 to 100,000 cycles per second. The potential delivered by it was approximately 100 volts at 30,000 cycles. The high voltage then had to be obtained by tuning a resonance circuit containing capacity and inductance to resonance with the generator. In this manner 4,000 volts were obtained at 30,000 cycles. This frequency, however, was too high for these experiments with the potentials obtainable. Accordingly, after a trial this method was also abandoned.

It was finally decided to attempt to utilize the resonance circuit of the Chaffee[11] Arc for obtaining the high frequency oscillation. This arc gives a nearly undamped sine wave and is quite simple to operate. The principle upon which the arc operates is described in detail in Professor Chaffee's original paper. It is an arc between copper and aluminum terminals in an atmosphere of hydrogen. The arc is operated in parallel with a condenser across a direct-current power main giving a potential difference of 530 volts. The discharge of the condenser across this arc results in unidirectional current surges through a primary coupling coil in series with the arc. The frequency of the surges is primarily determined by the capacity of the condenser and the current supply. This surge, acting upon the coupling coil of a secondary circuit, sets the latter into oscillation in its own period, as demanded by the nature of the constants of the secondary circuit. If the two circuits are tuned so that the primary discharge occurs regularly just in time to add its impulse to an oscillation of the secondary circuit in the proper phase to reinforce it, the resulting oscillations in the secondary circuit consist of a practically undamped train of waves. In practice, the discharges of the

primary are generally so arranged that they occur once for every three or four oscillations in the secondary. The effect of the secondary on the primary when they are in tune is in the nature of a trigger action tending to make the impulses come at the proper time.

III.

METHOD OF OBTAINING HIGH FIELDS AT HIGH FREQUENCIES.

The frequency desired in the arc circuit was in the neighborhood of 5,000 cycles per second with a potential of from 5,000 to 10,000 volts. The circuit perfected for this purpose is represented in Fig. 1. Because the energy output of the arc is small, and because as little damping as possible was desired, special precautions had to be taken to reduce dielectric absorption and resistance in the secondary circuit. R in the figure was a variable lamp bank resistance placed in the direct-current circuit. With it the current could be varied almost continuously from .2 to 2.5 amperes. C_1 is the primary discharge condenser, the magnitude of whose capacity regulated the frequency of the discharge through the arc. In this work it consisted of two 1 microfarad Western Electric telephone condensers, insulated to stand 1,000 volts alternating potential. L_1 was the primary of a small coupling coil wound with the wires of the primary and secondary in parallel. It was approximately 70 cm. long, 20 cm. in diameter, and had 110 turns of wire. The secondary of this coil is designated by L_2 in the diagram. L_2' consisted of a single large coil of 97 turns of No. 8 hard-drawn copper wire, wound on a hexagonal frame 95 cm. in diameter and 74 cm. long. The insulation on L_2' was ebonite throughout. The inductance of L_2 and L_2' together amounted very closely to 8×10^6 cm. C_2, the secondary condenser, was an air condenser having 150 galvanized iron plates 38 by 38 cm. square, each separated by about 3 mm. of air. The capacity of the condenser on measurement turned out to be 0.0863 microfarad. L_3 consisted of three large coils wound on dry sugar barrels covered with paraffined paper. In the winding No. 18 double cotton-covered wire was used. The coils when wound were thoroughly saturated with molten paraffine. The dimensions are given below. These were connected in series, end for end, and loosely coupled to the large secondary coil L_2'.

Coil.	Length.	Mean Diam.	No. Turns per Cm.
1.....	53 cm.	51 cm.	5.6 No. 16 wire.
2.....	54 cm.	53 cm.	8.0 No. 18 wire.
3.....	65 cm.	56 cm.	7.5 No. 18 wire.

The capacity of the tertiary condenser C_3 was .0042 microfarad and consisted of two "Navy" jars in parallel. The capacity of the tertiary circuit also included the distributed capacity of the large coils, the capacity of a Braun electrostatic voltmeter, the capacity of a small variable tuning condenser, and the capacity of the ionization chamber. The tuning was accomplished by varying the current in the primary arc circuit, by varying the primary condenser, and by varying the inductance picked off the secondary inductance coil. The frequency of alternation used was found to be 7,666 cycles per second when the ionization chamber was in the circuit.

The frequency of the alternating potential was determined by photographing the image of the spark in a revolving mirror. The speed of the mirror was varied from 2.5 to 10 revolutions per second. Two different cameras were used, one being a camera with a Cooke anastigmat. lens, $f = 3.5$. The distance between the sparks was determined by photographing a 10 cm. steel scale in the spark gap on the same plate with the sparks. The distance between the mirror and gap was varied from 158 cm. to 212 cm. and the distance between the camera and the mirror was also varied. The mean of fifteen different plates gave the frequency as being 7,666 cycles per second.

The potential was read on a Braun static voltmeter while the determinations were being made. The potentials varied from 4,150 volts to 4,650 volts. The voltmeter had a range of 10,000 volts, so that the readings were taken right at the center of the scale where they were most accurate. The voltmeter was calibrated.

IV.

Apparatus and Mobility Measurements.

The apparatus used in the mobility determinations was essentially the same as that of other observers who used this method. It had, however, some slight changes that were necessitated by the fact that neither the potential nor the frequency of the alternating potential could be varied through sufficiently wide limits. The determinations were accordingly made by varying the distance between the gauze and the plates, keeping the potential and frequency constant. The essential features of the apparatus, as well as the dimensions, are included in the diagram, Fig. 1. The ions were generated by means of a film of ionium on the brass plate I fastened beneath the gauze. The gauze was mounted on ring G, which was supported by a tripod set in a well-paraffined wooden block. Above the gauze the collecting plate K, surrounded by an earthed guard ring E was suspended parallel to it from an insulated

brass tube set in the supporting disc, P. The plate could be raised or lowered by means of a nut, N, which rotating against the collar C, engaged with a thread in the vertical rod of the collecting plate. To facilitate the lowering of the plate, a spiral steel spring S was fastened to the lower part of the collar and to the shoulder of the collecting plate. This pressed the nut firmly against the top of the collar. The pitch of the thread allowed the plate to be moved half a mm. for each complete turn of the nut. A bell-jar silvered inside covered the whole apparatus, making a close contact with the flat iron disc which served as a base. Through two amber plugs in the base, the wires to the accelerating fields were led in. The lower plate F of the accelerating field was placed three cm. below the gauze, and parallel to it. To enable the nut to be rotated with the bell-jar over it, a steel tube was set into the neck of the bell-jar. This had a hole in the center into which was ground a brass plug. At the lower end of the latter a prong projected that engaged with an amber cylinder projecting from the side of the nut N. The brass plug A could be rotated by means of a handle from the outside. Contact between the electrometer lead and collecting plate was made through an amber tube set in the brass plug A by means of a fine steel wire. This wire projected into a deep mercury cup drilled out of the center of the rod of the collecting plate. On top of the disc P were placed several small cups containing P_2O_5, which were carefully grounded. The orifice O in the base allowed the air to be withdrawn. All air that was admitted to the apparatus passed through a long drying train containing P_2O_5, H_2SO_4, and $CaCl_2$. The lead wires from the chamber went to a small ebonite commutator Z carefully insulated on paraffine. On the same base with the commutator were three small "flash light" batteries B' which gave a potential of 9 volts, and furnished an accelerating field for the ions of 3 volts per cm. The quadrant electrometer Y used in this work had a fine quartz suspension, and a sensibility of 1,500 mm. per volt.

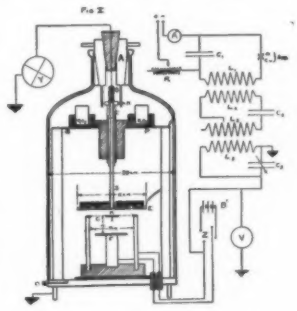


Fig. 1.

In making a determination the potential and the frequency of the alternating current were kept constant, and the distance between the plates was varied. The deflections of the electrometer corresponding to readings taken at various distances between the gauze and the plate were recorded. The deflections were due to the ions which had accumulated on the upper or collecting plate during the interval in which the

alternating potential was allowed to act on the ions. This period of collection varied for various determinations being usually about 15 or 30 seconds. If all the ions had a constant mobility, the theory would lead us to expect, on plotting these results with the deflections as ordinates and the distances as abscissae, that we should get a curve parallel to the X axis until the critical distance is reached which the ions are just able to traverse in the time of one half alternation of the field. At this

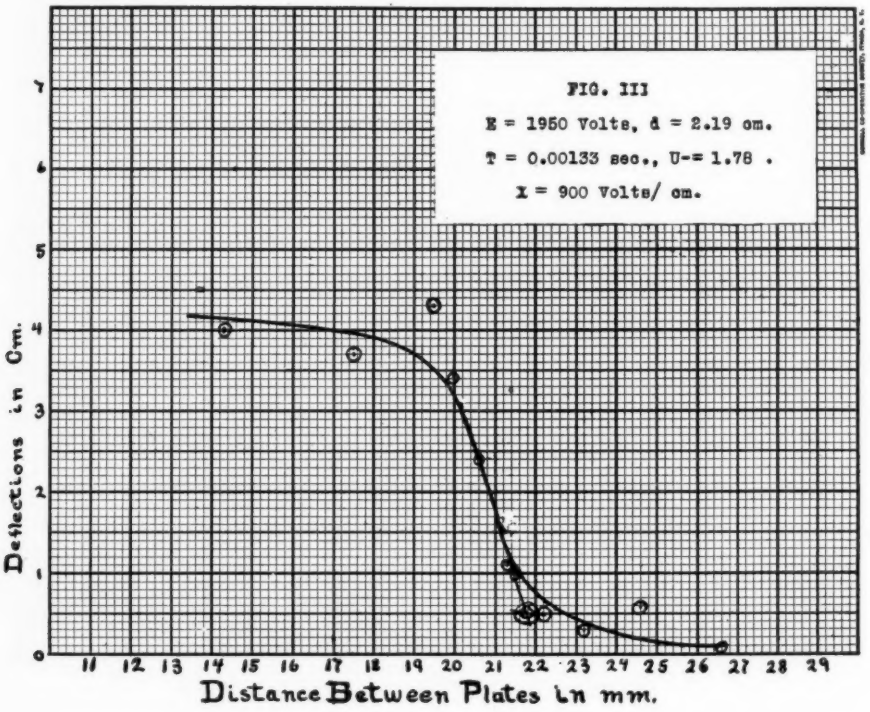


Fig. 3.

point the curve should drop abruptly to O parallel to the Y axis. In practice this is never actually the case, since first, the ions do not all start from exactly the same point in the meshes of the gauze. Further, the plate and the gauze are never exactly parallel. With the changing distance between the plates the distortion of the field due to outside influences might also change the value of the field strength. Finally, in plotting the deflections for the same time of charging of the plate, the assumption is made that the capacity of the electrometer and the collecting system is constant. This is actually not the case, for the capacity varies slightly with the distance between the gauze and plate. Thus, the deflections observed are not quite strictly proportional to the

number of the ions. All these factors round off the corners of the curves and cause the otherwise vertical line to be inclined at a slight angle with the vertical. A typical curve for one of the determinations for the commutator work is given in Fig. 3. The intercept of the curve with the X axis was chosen as the critical distance. This gives the

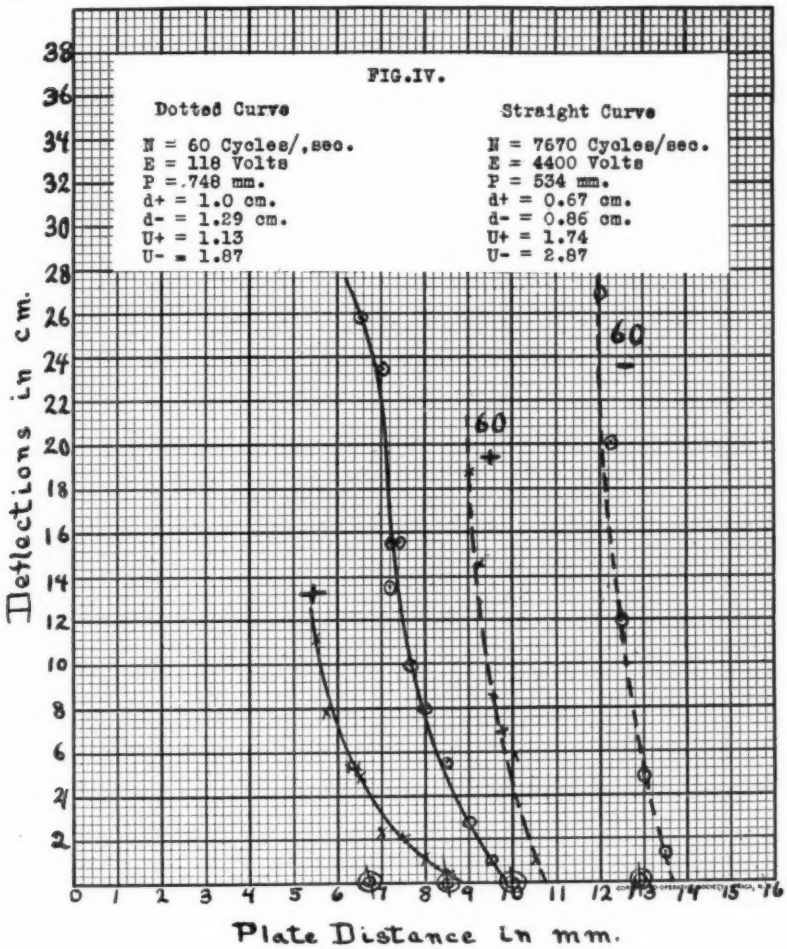


Fig. 4.

critical distance traversed by the ions that have been subjected to the most intense field, and which have come from the nearest point of the gauze. A typical set of curves for the determinations using the arc as a source of alternating potential, are given in Fig. 4. One pair was taken at the high potential with the high frequency alternating current, and correspond to the deflections of the positive and negative ions. The

curves marked 60 correspond to determinations on the positive and negative ions using the 120-volt 60-cycle city power alternating current. The only difference between these curves and the curves taken with the commutator is that the former show only the vertical element of the curve. This is due to the fact that in the work with the arc a greater sensitiveness was attained through the use of a more sensitive detecting instrument, and through the use of coarser gauze (10 meshes to the cm.). The time of collection of the ions with the arc was 15 seconds. The increased sensitiveness also caused the increase in prominence of the tails of the curves in these measurements.

V.

SOURCES OF ERROR.

The errors to which these measurements are subject may be classified under three heads. The first class may be designated as instrumental errors, which are due to the form of the ionization chamber. To this class belongs the lack of parallelism between the plate and the gauze, with its attendant distortion of the field, as well as the distortion of the field due to outside influences. The effects of these were, however, shown to be practically negligible in these determinations for reasons to be given later.

The distances between the plate and the gauze were measured by means of a cathetometer which gave them with an accuracy of 0.1 mm. This was more accurate than the determination of the critical distances from the curves, which could only be obtained within 0.3 mm. This amount of uncertainty was due to the tailing off of the curves near the X axis. In determining the critical distances from the curves these tails were ignored, the intercept being taken as the point where the continuation of the straight, downward part of the curve intercepted the axis of abscissae. To preclude the possibility of the existence of serious errors of the first class in the measurements of the mobilities, check determinations were made with the chamber using the 60-cycle 120-volt alternating potential from the city power mains. The mobilities thus obtained were found to be strictly normal, their values lying close to the mean of the best determinations by other observers, thus showing these uncertainties to be negligible.

The second class of errors is due to inaccuracies entering into the values of various constants of the alternating potential. The frequency of the oscillations was determined as previously described, with an accuracy of two per cent. either way.

A second source of uncertainty of this class lay in the fact that the

form factor of the alternating current from the arc was not determined. The mobilities were computed on the assumption that the alternating potential had the form of an undamped sine wave. The Chaffee arc is supposed to give such a wave. However, there exists the possibility of the presence of higher harmonics. These might change the form of the wave which would necessitate an alteration in the constant factor $\pi/\sqrt{2}$ in the mobility equation. This alteration for the extreme case of the transition from a sine wave of frequency N, to a square wave of the same frequency, measuring the potential with a static voltmeter, might lower the factor above by as much as ten per cent.

Possibly the greatest source of inaccuracy in the second class might arise through the variation of the potential given by the arc. This fluctuated nearly continually between the values 4,150 volts and 4,650 volts, as indicated by the static voltmeter. Each point of the curves between plate distance and deflection corresponds to a mean of from five to ten separate readings taken over an interval of 15 minutes. The curves through the points plotted were drawn so as to be as near the mean as possible. Consequently, the intercept of the curve with the axis of abscissæ, which determined the critical distance, corresponds to a potential difference which was very near the mean of 4,400 volts.

The last class of errors are those due to the improper drying of the air used in the determinations. The effect of careful drying was distinctly noticeable, and was in all probability the greatest cause of variation of the experimental results recorded. In the first experiments with the arc circuit the air was not carefully dried, the air being passed through only a short drying train. The later determinations were made on air that had passed through a long drying train containing $CaCl_2$, H_2SO_4, and P_2O_5. In some of the later determinations notably those at about 430 mm. pressure (see Table II.), the air had stood over P_2O_5 for several days before being used. In general it may be stated that the lower values of the mobilities recorded in the table, pertain to measurements made with imperfect drying.

VI.

RESULTS.

The results obtained by the commutator method are given in Table I.

In the first column are the frequencies of alternation; in the second are the critical distances. In the third and fourth columns the mobilities of the positive and the negative ions are calculated from the formula $U = d^2N/V$; in which d = critical distance, N = frequency of alternation in one half cycles per second, V = potential. The last column gives the values of the field strengths at the critical distances in volts per

TABLE I.

Ionic Mobilities Obtained with the Commutator, Winter 1914.

N.	*d.*	*U+.*	*U—.*	*X.*
60	1.12	1.38		96.0
428	0.86	1.45		257.0
747	0.87	1.26		514.0
625	1.42	1.39		698.0
740	1.82	1.50		990.0
60	1.26		1.780	94.0
650	1.56		1.795	618.0
706	2.12		1.960	720.0
725	2.17		1.880	900.0

cm. The pressures were in all cases the atmospheric pressures at the time the measurements were taken. No precautions as to drying the air were taken in these early commutator experiments.

The results show that for fields ranging from 90 volts per cm. to 900 volts per cm. there is no certain abnormal increase of the mobility of either ion. Further, it should be noted that in these determinations there is no tendency for the negative ion to increase its mobility relative to the positive ion, as would be expected should the negative ion begin to break up at the highest potential used.

The results obtained with the arc are tabulated in Table II.

TABLE II.

Ionic Mobilities Obtained with Chaffee Arc, Winter 1916.

N.	*d+.*	*d—.*	*u+.*	*u—.*	*P.*	*U+.*	*U—.*	*X+.*	*X—.*
60	0.99	1.38	1.10	2.12	760 mm.	1.10	2.12	121	87
60	1.00	1.26	1.13	1.78	756 mm.	1.12	1.76	120	96
60[1]	1.00	1.28	1.13	1.85	748 mm.	1.12	1.84	118	93
60	1.33	1.56	1.95	2.70	578 mm.	1.48	2.05	91	77
		Mean mobilities at			760 mm.	1.21	1.94		
7,670	0.50		0.97		750 mm.	0.98		12,450	
7,670	0.55	0.64	1.17	1.59	746 mm.	1.19	1.62	11,450	9,750
7,670	0.54	0.61	1.07	1.37	747 mm.	1.09	1.40	11,550	10,000
7,670	0.50	0.65	1.25	1.80	735 mm.	1.28	1.86	12,450	9,600
7,670	0.66	0.84	1.70	2.74	534 mm.	1.27	1.95	9,580	7,430
7,670[1]	0.78	1.02	2.36	4.04	436 mm.	1.36	2.32	8,000	6,000
7,670[1]	0.85	1.01	2.72	3.88	430 mm.	1.54	2.18	7,346	6,160
7,670	0.82	1.10	2.58	4.29	416 mm.	1.41	2.29	7,610	5,670
7,670	0.85	0.90	2.67	3.07	384 mm.	1.35	1.53	7,340	6,910
7,670	0.80	0.86	2.51	2.90	382 mm.	1.26	1.46	7,800	7,260
7,670[2]	1.11	1.22	4.78	5.80	304 mm.	1.96	2.32	5,610	5,160
		Mean mobilities at 760 mm.				1.33	1.89		

[1] These readings were taken with very dry air.

[2] The value of the positive mobility only estimated here, not determined.

The determinations of the positive and negative mobilities were made simultaneously by changing the commutator of the accelerating field. In the first column are the frequencies of alternation. In the second, the critical distances, and in the fourth, the pressures in mm. of mercury are given. The third column contains the mobilities of the ions as calculated from the formula for a sine wave alternating current, *i. e.*, $U = \pi N d^2/\sqrt{2}E$, where E is the potential given by the electrostatic voltmeter, N the frequency, and d the critical distance. The fifth column contains the mobilities of both ions reduced to 760 mm. pressure. In the last column the field strengths under which the determination was made, are given in volts per cm. for the maximum value of the alternating field.

The range of pressures worked with extended from 750 mm. to 300 mm. of mercury. The work could not be carried to higher field strengths at this frequency with the arc, for at a distance of about 4 mm. at atmospheric pressure occasional sparking began between the plates. The potential difference between the plate and the gauze as registered by the electrostatic voltmeter was but 4,400 volts, when sparking began at a distance of 4 mm. According to all results obtained on the sparking potentials at atmospheric pressure by the various observers, the potential difference which a static voltmeter would read, when sparking took place at 4 mm., should, with the alternating potentials, be about 10,000 volts. This sparking was therefore in all probability due to occasional momentary irregularities in the operation of the arc, which would allow the potential to reach a value as high as 10,000 volts. This effect would not invalidate the mobility determinations, for the number of ions driven to the plate through such an occasional irregularity would not be great enough to sensibly affect the electrometer. They might, however, possibly augment the tails of the curves. This sparking limited the pressures to which the experiments could be pushed for the following reason: The point where the positive ions could just be detected was just 1.5 mm. away from this sparking point, *i. e.*, at about 5.5 or so mm. Now the distance over which a spark will pass varies inversely with the pressure, voltage being constant. The distance at which the ions can just be detected varies as the square root of the mobility. But the mobility varies inversely as the pressure, and, therefore, the distance at which the ions may just be detected varies inversely as the square root of the pressure. The result is that the pressure was not far distant, with the frequency used, at which the sparking began to encroach on the distance at which the ions might be detected. This occurred at about 300 mm., the mobilities of the positive ions measured at this pressure being quite unreliable due to the sparking. The mean of the

determinations are 1.33 for the positive ions and 1.89 for the negative ions. The field strengths corresponding to the maximum value of the potentials used range from 12,450 volts per cm. down to 5,160 volts per cm. They all agree in showing that *neither the mobility of the positive nor of the negative ion shows any tendency to abnormal increase* for the pressures and field strengths worked with. Further, it can be seen that the *negative ion shows no tendency to increase in mobility over the positive ion*, as it should do, did it start to break up.

VII.

Discussion of Results.

The results on the positive ions obtained in high fields at high pressures in air seem on the basis of the "cluster" theory to be in direct contradiction with the results of Todd[6, 7] who worked with positive ions at very low pressures and low voltages. The "cluster" theory demands that for a sufficiently high value of the product, mean free path times field strength, the positive ion should show an abnormal increase in mobility. This apparently occurred in the case of Todd's experiments at a value of $X/p = 2.6$, where for the sake of convenience we represent the value of field strength times mean free path by the ratio of X/p to which it is proportional, letting X be the field strengths in volts per cm. and p the pressure in mm. of mercury. The writer worked on positive ions with pressures as low as 300 mm. and with ratios of $X/p = 18.0$ and yet found no abnormal increase in the mobilities. This means that with these values of X/p, ranging from 0.1 to 18.0, the cluster, if it exists, shows no tendency whatever to break up. Beyond the range of these experiments, which was limited by the irregularities in the operation of the arc, the ion cluster might conceivably break up.[1] The range of X/p where this might occur extends from $X/p = 18.0$ to $X/p = 39.6$. At the latter point sparking occurs between parallel plates at a pressure of 760 mm. Ionization by collision must take place somewhere between these limits. The exact point where this occurs for the positive ions has not been determined to the best of the writer's knowledge. Since it is obvious that the positive ion cluster must begin to disintegrate before the value of ionization by collision by positive ions can occur, it is also obvious that the values of X/p worked with are close to the threshold of the value where the ions must begin to disintegrate, if they disintegrate at all. One may consequently assert that at atmospheric pressures in air the ions show no tendency to abnormal mobilities in fields which should be great enough to cause a cluster ion to break up. This con-

[1] The premature sparking is presumably not to be attributed to the behavior of the ions, since the irregularities in the operation of the arc are entirely sufficient to explain this action.

clusion is in excellent accord with the recent results of Wellisch[13, 14] obtained on the mobilities of positive ions at very low pressures, *i. e.*, 0.05 mm., with low potentials. He found that at values of X/p as high as 34.5 and higher, the mobility of the positive ions was constant, and very nearly equal to that found by all observers at high pressures. This value of X/p was very nearly equal to that causing ionization by collision to begin for the negative ions at those pressures, according to Townsend's data.

The results of the writer on the negative ions taken at high pressures and with high fields appear at first sight to be at variance with the results of the observations at low pressures. On the basis of the results at low pressures and the cluster theory Townsend[12] in his recent book (Electricity in Gases), comes to the conclusion that the breaking up of the negative cluster takes place at values of $X/p = 0.1$. He further asserts on the basis of some results of Lattey[5] that this break-up point for lower pressures at least is a function of X/p. It is true that the apparent break-up point in the results of most observers at pressures below 10 cm. of mercury does occur at a value of X/p about equal to 0.1. However, such a break-up point is not in any sense a function of X/p alone. This became at once evident to the writer when, in view of his results, he worked over the data of Kovarick[4] on the breaking up of negative ions at low pressures. The break-up point was found to be more nearly a function of p alone than of X/p. This may be seen from Table III., which gives the values of X/p of some observers, and the results obtained by them as regards the mobilities of the ions.

TABLE III.

Observer.	X/p.	Pressure.	Mobility.
Lattey[5]	.06	28.0 mm.	Abnormal − ion.
Kovarick[4]	.15	510.0 mm.	Normal − ion.
Kovarick[4]	.053	11.4 mm.	Abnormal − ion.
Todd[6]	2.6	.79 mm.	Abnormal + ion.
Writer	.128	750.0 mm.	Normal − and + ions.
Writer	1.2	750.0 mm.	Normal − and + ions.
Chattock[9]	4.0	760.0 mm.	Normal − and + ions.
Writer	13.0	746.0 mm.	Normal − ions.
Frank[10, 18]	13.0	760.0 mm.	Abnormal − and + ions.
Writer	16.6	750.0 mm.	Normal + ions.
Writer	17.0	304.0 mm.	Normal − ions.
Writer	18.3	304.0 mm.	Normal + ions.
Wellisch[13]	34.6	.87 mm.	Normal + and − ions.
Townsend[12]	38.0	4.1 mm.	Beginning of ionization by collision.
Bishop[15]	40.0	100.0 mm.	
.....	39.5	760.0 mm.	Sparking potential in air.

Besides the values of X/p and the names of the observers, the pressures in mm. of mercury are given at which the determinations were made. The table also includes the values of X/p for ionization by collision, and for sparking at atmospheric pressure. The conclusions of Townsend are further shown to be at variance with the results of the writer who determined the negative mobilities at pressures as low as 300 mm. and at values of X/p as high as 17 without finding the least indication of an abnormal increase in the absolute value of the mobility of the negative ion. Even if these results as to the absolute values of the mobilities were quite inaccurate, the fact that the negative ions show no increase in mobility relative to the positive ions would indicate the absence of the disintegration of a negative cluster. One must conclude that the apparent breaking up of a negative cluster observed at the low pressures by the other observers is in reality not a breaking up of the cluster at all, for it does not obey the laws which such a breaking up should obey. The explanation of the abnormally high mobilities at low pressures must then be looked for elsewhere. It was stated in the introduction that it is conceivable that the very mobile negative electron might under certain circumstances exist in a free state and enter into the determinations of the mobilities. That this actually occurs at very low pressures has been shown by Townsend and Tizard.[20] If the free electron exists at intermediate pressures, the following statements may be made concerning it. It did not appear in appreciable numbers in the results of the writer at the pressures with which he worked. Further, it must be concluded that the appearance of the free electron is not primarily a function of X/p. Finally, its appearance seems to depend on the pressure alone. The pressure where it appears in a gas might also depend on the chemical nature of the gas. The existence of free negative electrons was ascertained for the pure gases, helium by Franck[20, 18] and nitrogen and hydrogen by Haines,[16] at atmospheric pressure. Wellisch[13] found that for air the free electrons make their appearance below 8 cm. of mercury in quantities great enough to detect. The conclusions stated above again agree in a striking manner with those arrived at by Wellisch from his experiments on the mobilities at very low pressures, and low potentials. Besides the free negative electrons which he detected at the lower pressures, Wellisch found perfectly normal negative ions down to pressures as low as 0.15 mm. mercury. These negative ions had mobilities strictly inversely proportional to the pressure, even though the value of X/p was as high as 34.5. He found that as the pressure was reduced, the relative number of the free electrons to the normal ions increased. No ions of intermediate mobility were detected. The

apparent increase of the mobility of the negative ions at pressures of about 10 cm. and below observed by most workers may therefore be ascribed to the fact that their methods were not sensitive enough to detect the free electrons as such. They thus obtained as mobilities a sort of fictitious mean mobility between the mobilities of the normal negative ions and the free electrons. These fictitious mobilities increased with decreasing pressure due to the greater proportion of free electrons present.

The results obtained by the writer on the mobilities of the positive and the negative gas ions at atmospheric pressures with high fields, lead to the conclusion that over a considerable range of field strengths the ions in air at high pressures show no tendency to break up. Considering the extent of the range worked with, and also considering the results of Wellisch over an equally great field at low pressures and low potentials, with which these results are in excellent agreement, one is forced to question the validity in the "cluster" theory, which until now has been that most generaly accepted.

In conclusion the writer wishes to express his great appreciation for the advice and encouragement given him by Professor R. A. Millikan, at whose suggestion the problem was undertaken. The writer's thanks are due to Professor E. Leon Chaffee for his kind suggestions concerning the operation of the arc, and to Mr. Kia Lok Yen for his valuable assistance in surmounting the considerable technical difficulties encountered in the latter part of the work.

Summary.

1. Utilizing the resonance circuit of the Chaffee arc as a source of alternating potential difference, and utilizing the Rutherford alternating current method of measuring mobilities, the mobilities of the positive ion were measured in fields nearly powerful enough to cause ionization by collision in air at atmospheric pressure. The mobilities were found to be perfectly normal within the limits of experimental error.

2. The mobilities of the negative ions were measured under the same conditions. No change in the absolute value of the mobilities of the negative ions could be detected, nor could any change in the mobilities of the negative ions relative to the positive ions be detected.

3. The results are in agreement with the recent results of Wellisch obtained at low field strengths and very low pressures, in leading one to the conclusion that the "cluster" theory of the ion is no longer tenable.

REFERENCES.

1. M. Langevin. Thesis, 1902.
2. E. M. Wellisch. Trans. Roy. Soc., *A*, 209, 1909.
3. W. Sutherland. Phil. Mag., 18, 341, 1909.
4. A. F. Kovarick. PHYS. REV., 30, 415, 1910.
5. R. F. Lattey. Proc. Roy. Soc., *A*, 84, 1910.
6. Todd. Phil. Mag., Ser. 6, Vol. 22, p. 791, 1911.
7. Todd. Phil. Mag., June, 1913.
8. J. S. Townsend. Proc. Roy. Soc., *A*, 85, 1911.
9. Chattock. Phil. Mag., 48, 401, 1899.
10. J. Franck. Ann. der Physik., 21, 972, 1906.
11. E. L. Chaffee. Proc. Am. Acad. Arts & Sc., Nov., 1911.
12. J. S. Townsend. Electricity in Gases, Oxford, 1914.
13. E. M. Wellisch. Am. Jour. Science, May, 1915.
14. E. M. Wellisch. Phil. Mag., March, 1916.
15. Bishop. PHYS. REV., December, 1911.
16. Haines. Phil. Mag., November, 1915.
17. Rutherford. Proc. Camb. Phil. Soc., IX., 1898.
18. Franck. Jahrb. d. Rad. u. Elect., IX., No. 2, May, 1912.
19. Franck and Pohl. Verh. d. Deutsch. Phys. Ges., 9, 69, 1907.
20. Townsend and Tizard. Proc. Roy. Soc., *A*, 87, 1912; *A*, 88, 1913.
21. Franck. Ver. d. Deutsch. Phys. Ges., 12, 1910.
22. Moore. PHYS. REV., 1912.
23. Rutherford. Radioactive Substances and their Radiations, p. 56.

THE PROPERTIES OF SLOW CANAL RAYS.

BY A. J. DEMPSTER.

THE following paper contains an account of experiments with positive rays under more varied pressure conditions and of slower speed than those generally used. In the usual canal ray tubes the potential is limited very largely by the vacuum; for instance, if the pressure is about 0.005 mm. of mercury, the potential with ordinary tubes is of the order of 20,000 volts. In this investigation the subject was first approached from the side of the light emission and later the analysis by electric and magnetic deflection was made.

LIGHT EMISSION.

The first to examine the light excited by slow positive rays was Stark.[1] He arranged a secondary cross field in the negative glow in a usual discharge tube; in this way he obtained a luminosity behind a hole in the secondary cathode, when the cross field was as low as 50 volts. Wehnelt[2] found that if a hole were made in a hot lime cathode, slow canal rays were obtained down to potentials of 50 volts. They were, however, so diffuse that no measurements could be made on them. In some experiments carried out by the writer[3] on the light excited by electrons, a Wehnelt cathode with potentials up to 4,000 volts was used, and it was observed that very strong positive rays passed backwards past the side of the platinum strip.

This method of ionizing the gas by means of electrons from a Wehnelt cathode was used in the present experiments and found to afford the following experimental advantages, namely, *the possibility of producing positive rays of any desired speed in a constant vacuum, and the possibility of changing the pressure over a wide range with constant speed of the rays.*

The cathode used in the following experiments had usually the shape shown in Fig. 1. The platinum strip 0.001 mm. thick and 1 mm. wide was clamped below the thin plates shown and the two halves of aluminum or brass were insulated by pieces of glass *a*, *b* fitted tightly into slots at

[1] J. Stark, Ann. d. Physik, 13, p. 390, 1904.
[2] A. Wehnelt, Ann. d. Physik, 14, p. 464, 1904.
[3] A. Dempster, Ann. d. Physik, 47, p. 796, 1915.

the edges. A plate P with a row of holes in it was screwed to the one half and insulated by the pieces of glass c, d. The heating current was brought in by the rods R, S.

In the first experiments to be described, an arrangement of cathode and anode similar to Fig. 2 was used. The whole fitted into a glass

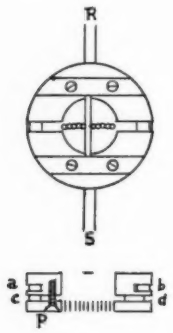


Fig. 1.

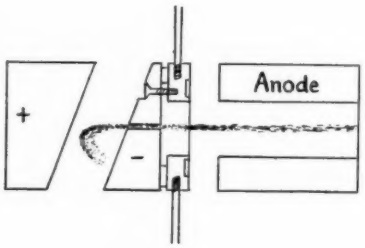


Fig. 2.

tube 4 cm. in diameter, and the rods leading in the heating current and brass caps to close the ends of the tube were made air tight by sealing wax. The cathode was made by heating a mixture of Ba, Sr and Ca nitrates on the platinum strip. By allowing hydrogen to stream in through a long fine capillary, while a Gaede pump was running, impurities were removed and pressure conditions were kept constant. To obtain the rays distinct it is important to remove mercury vapor and any other vapors present; this was done by means of a U-tube immersed either in liquid air or a mixture of solid carbon dioxide and alcohol.

THE POSITIVE RAYS.

When the pressure is low, 0.001 mm. of mercury or less, the positive rays issue from the back of the cathode as a luminous bundle of bluish light at all potentials from 40 volts between the middle of the cathode and the anode up to 2,000 volts. As the potential is decreased below 100 volts the luminosity becomes gradually very faint and it is only with new cathodes that luminosity at the lowest potentials can be observed. As the cathode gets old and needs to be heated hotter, it is necessary to apply higher voltages up to perhaps 150 volts or more before the positive rays become visible. This is possibly due to the fact that when the cathode gets old the electron stream comes from a greater area of the strip instead of from a small point. This greater density of charge displaces the fall of potential to the neighborhood of the anode where the lines of force do not accelerate the positives in the

proper direction. *The rays in these high vacua may be stopped entirely by an opposing field and may be completely deflected and bent into a parabola by an inclined field* as indicated in Fig. 2. It may be observed that in contrast to the behavior of electrons[1] the parabola is continuous up to its apex, indicating that the positive rays can excite light when slowed up to a speed of a few volts. This was tested by stopping 48-volt rays by directly opposing potentials. It was observed that, with 52 volts opposing, a dark space was just noticeable before the plate to which the potential was applied. We thus conclude that *positive rays can cause light when moving with a speed less than that corresponding to 5 volts.* Probably much slower rays also excite light, but it was not possible with the arrangement used to prove it. These positive rays at potentials of several hundred volts excite the hydrogen series lines, but, as they were too faint at the lowest speeds for a spectrum photograph, it is impossible to say whether or not the hydrogen series lines are excited or emitted by the slowest rays.

For fast rays (20,000 volts and up) the evidence is not conclusive. Koenigsberger and Kutchewski[2] find that the positive bundle deflected out by a magnetic field excites no light, although causing fluorescence on the wall. Dechend and Hammer[3] make the same observation. Baerwald[4] however deflected out a luminosity from the rays. The Doppler effect also shows that rays above a certain speed do not excite light. The fact that slow positive rays are able to cause light needs to be considered as a possible complication in experiments on the lower limit to the speed at which electrons excite light, especially if the vacuum used is not low and if any form of arc is used.

The Neutral Rays.

When the pressure is increased to about .005 mm. of hydrogen, the phenomena are more complicated. Instead of the striking sharp break in the luminosity when the positives are stopped and turned back by an opposing field, there is merely a sudden decrease in the light and a luminosity continues right up to the opposing plate. This luminosity could be due to negative particles, electrons or neutrals and to decide the matter a condenser was arranged to deflect the rays sideways as shown in Fig. 3. It was found that the positive bundle was deflected but there still remained an undeflected bundle of neutral rays. No negatively charged atoms were observed; if the holes were large, however, electrons

[1] E. Gehrcke and R. Seeliger, Verh. d. D. P. G., 14, p. 335, 1912.

[2] J. Koenigsberger and J. Kutchewski, Phys. Zeit., 11, 379, 1910.

[3] H. v. Dechend and W. Hammer, Sitz. d. Heid. Akad., 21 abh., 1911.

[4] H. Baerwald, Ann. d. Physik, 34, p. 883, 1911.

appeared as observed by Wien[1] for fast canal rays. A photograph of the tube showing the deflected and undeflected bundle is given in Fig. 3*a*. The appearance was the same at all potentials down to 50 volts. That the light is due to neutral rays which were neutralized before reaching the condenser and not to resonance radiation caused by light from the electron discharge was proved by the fact that when a similar slit was made in the anode and the issuing electrons were deflected, no undeflected luminosity remained. *These neutral rays in hydrogen are still able to excite light when moving with a speed corresponding to a potential of 50 volts.* This speed, according to my observation, is a rather sharp lower limit to the speed at which they can excite light, for with rays a few volts slower the neutral bundle could not be detected, although the positive bundle was unaltered.

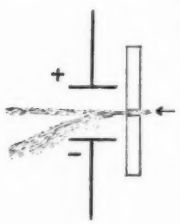


Fig. 3.

This behavior of the neutral rays offers a possible explanation of the dark space between the displaced and undisplaced lines in the Doppler effect in canal rays; the slow positive rays are soon neutralized and the slow neutrals are not able to excite light. The observed value for the minimum velocity in the Doppler effect is given by Stark as $1{,}07.10^7$ cm. per sec. for H_a, corresponding to a fall of the hydrogen atom through 57 volts, while the lower limit for excitation by the neutral rays observed above was 50 volts.

The changes that occur in hydrogen as the pressure is gradually diminished, while the potential is kept constant, are as follows: at high pressures (.05 mm.) there is a strong bundle which is quite unaffected by a deflecting electrostatic field, due probably to the fact that it consists mostly of neutrals. As the pressure is decreased the bundle becomes fainter and a positive deflected beam becomes visible. The two beams are of approximately equal strength at .005 mm. As the pressure is still further decreased, the neutral bundle becomes fainter till at the highest vacua only the positive remains.

The fact that the neutral rays excite light is not in agreement with the theory given by J. J. Thomson[2] or in fact with the ideas underlying Bohr's atom model. These theories regard the emission of light as taking place during the return of an electron to a positive center; the dark space in the Doppler effect is accounted for by J. J. Thomson by assuming that below a certain speed neutral particles are not ionized so that they can never act later as light emitters. On

[1] W. Wien, Wied Ann., 65, 446; 1898.
[2] J. J. Thomson, Positive Rays, p. 99.

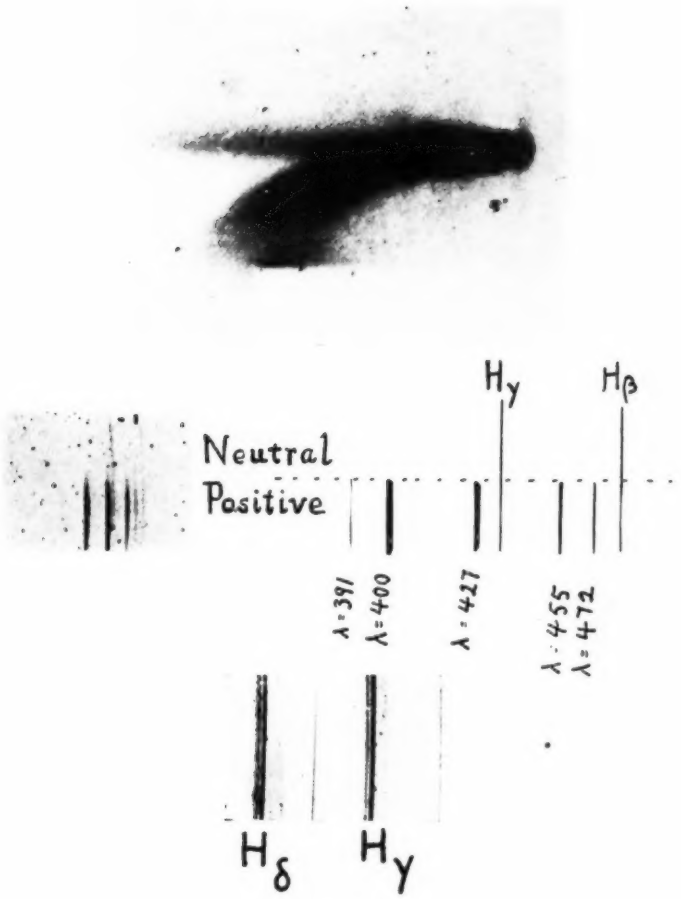


FIG. 3a.

A. J. DEMPSTER.

these theories, however, if we make the vacuum so high that changes take place slowly and then remove all the positives at one place, there should be no luminosity until more positives have been formed from the neutral bundle. This is not the case and the view is preferable that the collision of the neutral particles causes light directly.

SPECTRUM OF THE TWO BUNDLES.

To determine whether the hydrogen series' lines were excited by the neutral or by the positive rays, photographs of the spectrum were made. The two bundles were projected across the slit one above the other so that the spectra of both could be taken simultaneously. A single large prism was used with large lenses of short focal length. With rays of 1,500 volts' speed, exposures of 2–4 hours were necessary. A reproduction and key is given on Fig. 3*a*. *The hydrogen series lines were found in both positive and neutral bundles.* In the positive bundle were five other strong lines or bands of which one is probably the strong barium line at $\lambda = 4{,}554$, the two at $\lambda = 472$ and $\lambda = 427$ agree with the strong positive bands shown in Fulcher's photographs[1] of electron excitation in air and the other two also agree with nitrogen bands. They are only excited by the positive rays and stop sharply at the neutral bundle while H_β and H_γ are equally strong in both.

CHANGE OF NEUTRALS INTO POSITIVES.

Since the neutral rays emit the hydrogen series lines, it is of interest to see if the light emission is accompanied by a changing into positive particles. J. J. Thomson regards this phenomenon as taking place when the speed of the neutral particle relative to an electron at rest is greater than that required by an electron to ionize the particle and his experiments indicate that the neutral hydrogen atom does not change into positive unless its velocity is greater than that corresponding to a fall through 20,000 volts, the ionizing speed for electrons. Wien,[2] however, finds a formation of positive from neutral rays in oxygen and nitrogen; and also in hydrogen when the potential was only 3,500 volts.[3]

The arrangement shown in Fig. 4 was used. In a vacuum of .01 mm. of hydrogen, 800-volt rays entered at S_1. E_1 deflected out the positives while the neutrals passed on through a second slit S_2. If any neutrals changed into positives, they were deflected by E_2 up into the chamber F and detected by an electrometer. It was found however that F always

[1] G. S. Fulcher, Phys. Zeit., 13, p. 1137. 1912.
[2] W. Wien, Ann. d. Physik, 39, p. 529, 1912.
[3] W. Wien, Ann. d. Physik, 27, p. 1030, 1908.

gained a positive charge, due either to slow positives diffusing in or to electron emission from F. This was avoided by raising F to a positive potential of 258 volts above the metallic chamber; it then gained a negative charge, and only fast positive rays would be able to enter it and charge it positively. As the potential of E_2 was increased F still gained a negative charge till E_2 became 180 volts. From 180 to 300 volts it gained an increasing positive charge, while further increase to 470 volts decreased the positive charge to zero, and, with higher potentials

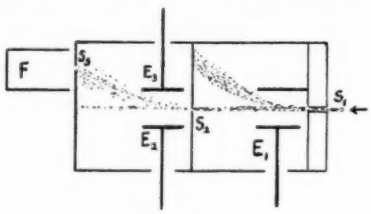


Fig. 4.

on E_2, F gained a negative charge again. This is what would happen as rather diffuse fast positive rays were deflected past the slit and so it is probable that neutral rays of 800 volts' speed are able to turn into positive rays. In view of the possibilities attending such changes, such as the absorption or emission of quanta of energy by a neutral in the brief period of its flight, the ejection of fast electrons, or the splitting up of the molecule, and the dependence on the speed of the rays it is hoped to investigate the matter further.

Doppler Effect.

Five photographs were taken of the Doppler effect in the hydrogen series lines H_β, H_γ, H_δ with rays of 3,000–4,000 volts and various pressures above .004 mm. A single Rutherford prism was used with lenses of 4 cm. aperture and 34 cm. focal length. No difference could be detected in the appearance of the undisplaced and displaced lines from that obtained with the usual method of exciting the rays. A reproduction of H_γ and H_δ is given in Fig. 3*a*, showing the Doppler effect to the left of the undisplaced line.

Ionization.

Ionization curves were made with an apparatus the same as in Fig. 4, except that the Faraday chamber and opening S_3 were opposite S_2. E_2 was connected to an Edelman electrometer and brought to various potentials relative to E_3 and the chamber. Positive rays or neutral rays of various speeds were allowed to enter through S_2 and the ions they made driven to E_2. With the positive and neutral rays together,

curves similar to that in Fig. 5 were obtained, where the abscissæ give the potential in volts forcing the ions formed to the electrode E_2, and the ordinates the numbers of negative ions obtained. Here the rays were 480-volt rays in hydrogen of .003 mm. pressure. There is an apparent saturation at about 30 volts but the continuation of the curve in Fig. 6 shows a second rise with final saturation at about the same potential as that used to give the rays their velocity.

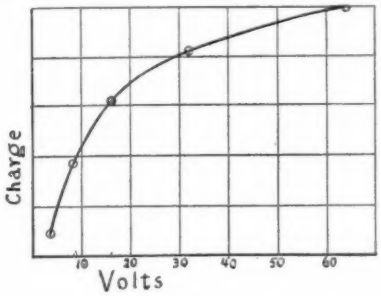


Fig. 5.

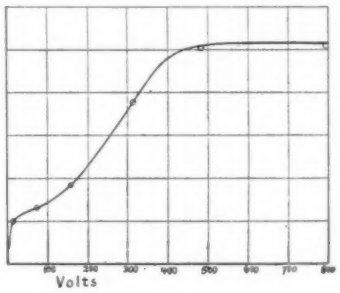


Fig. 6.

When the positives were deflected out by E_1, and only the neutrals and any newly formed positives allowed to enter the condenser, curves similar to Fig. 7 were obtained. This curve was for 480-volt rays in hydrogen at .0057 mm. pressure, and shows the positive charge obtained on E_2 as the potential difference was increased. The curve for the negative charge obtained was almost identical; the negative charge was, however, much greater, but could be reduced to approximate equality by a magnetic field. This indicates the presence of electrons, but a reason for the slow saturation can not be given at present. With fast canal rays an absence of saturation has been observed by Seeliger[1] and Baerwald[2] and ascribed to ionization by collision.[3]

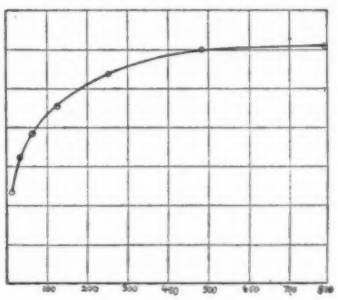


Fig. 7.

[1] R. Seeliger, Phys. Zeit., 12, p. 841, 1911.

[2] H. Baerwald, Verh. d. D. P. G., 16, p. 790, 1914.

[3] The assumption that the impact of positive rays can cause the emissions of fast electrons of the same energy would account for the form of the curves and agree with the conclusion recently reached by A. W. Hull (PHYS. REV., 7, p. 16, 1916), since it was found above that positives excite a radiation when their energy is of the order of magnitude of that required for electrons to excite light, we could assume that electrons are ejected under the influence of radiation excited by the impact of the positives, the maximum frequency of the radiation being given by, $h\nu$ = energy of the positive particle.

DEFLECTION IN ELECTRIC AND MAGNETIC FIELDS.

The electric and magnetic deflection of slow positive rays from gases have been examined thus far only by J. J. Thomson[1] and by Knipp. In J. J. Thomson's experiments the rays after falling through a potential difference of from 160 to 420 volts, were deflected in a magnetic field and m/e computed from the measured deflection and the volts. The result of these experiments was to detect the presence of hydrogen atoms and of particles for which m/e was from 25 to 44 times as large. Knipp[2] examined the rays from a Wehnelt cathode and found that 150-volt rays were not fast enough to affect a photographic plate without being accelerated by about 1,500 volts. These slow rays were therefore accelerated and then analyzed by electric and magnetic fields and values of m/e which corresponded to hydrogen atoms, hydrogen molecules, and doubly charged carbon atoms were found.

The method employed in the present experiments was to deflect the original slow rays by both electric and magnetic fields and to detect the deflected rays by the charge they carry. This method of detection has been previously used for fast canal rays by J. J. Thomson.[3] The apparatus is shown 4/10 actual size in Fig. 8. The analyzing chamber was

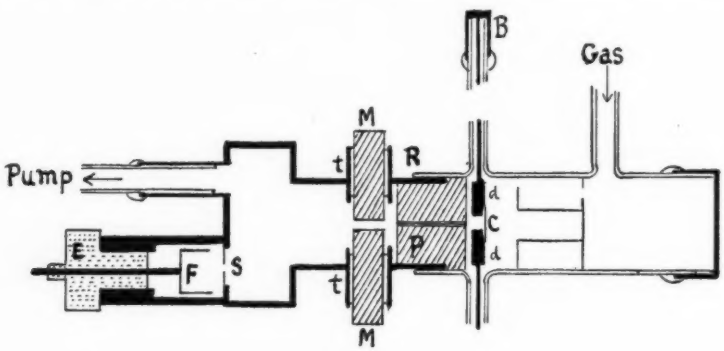


Fig. 8.

made completely of brass to avoid any static charges since the slow rays are very easily deflected. The Faraday chamber F was supported by an ebonite plug E which was made airtight by picien. The entrance to the Faraday chamber was through a parabolic slit S about 9 mm. long and 1 mm. wide, the minimum electrostatic deflection being about 7 mm. The iron pole pieces M fitted tightly into glass tubes and were sealed by De Khotinsky cement. The glass tubes, which did not pro-

[1] J. J. Thomson, Phil. Mag., 16, p. 673, 1908; Phil. Mag., 18, p. 838, 1909.

[2] Knipp, Phil. Mag., 22, p. 926, 1911, PHYS. REV., 34, p. 215, 1912.

[3] J. J. Thomson, Phil. Mag., 24, p. 245, 1912.

ject into the chamber, were similarly sealed into tight-fitting brass tubes t soldered into the walls of the chamber. The canal 0.7 mm. in diameter and 3.5 cm. long was a drawn copper tube set in an iron plug P. The cathode C was at first made as in Fig. 1 and 2, but, later, one has been used which is more easily made; the two brass pieces d were held in place and insulated by means of two dowel pins of glass not shown in the figure. The heating current is led in by rods soldered to brass caps B, which are made tight by sealing wax. It was found that the soldered joints in the chamber soon leaked after being warmed and cooled a few times during the removal and resealing of the glass tube

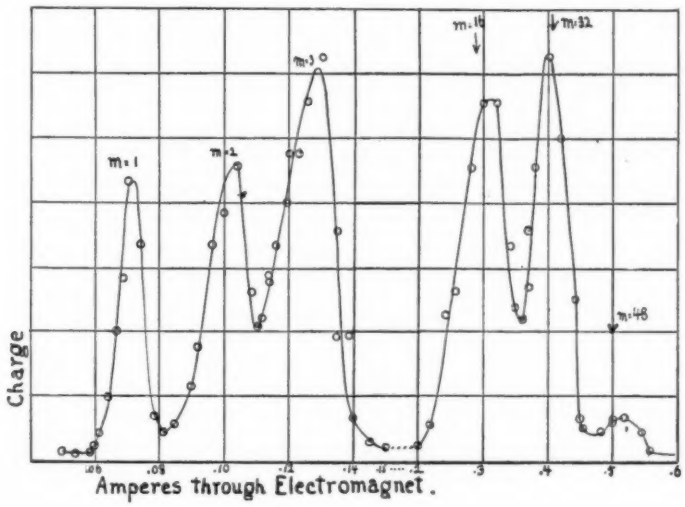


Fig. 9.

at R, the joints were then coated with shellac. It would, however, be an advantage to have the analyzing chamber half as large and the whole enclosed in a glass tube.

The magnetic field was produced by an electromagnet whose poles were brought against the iron pieces set in the chamber, and the PD necessary to deflect the parabolas electrostatically was applied to the iron pieces. The electron stream in front of C was shielded from the poles M by a screen at the iron plug consisting of 6 plates of transformer iron at right angles to the tube, also by several pieces bent around the tube itself. As the current through the electromagnet was increased bringing successive constituents of the rays into the Faraday chamber, the charge obtained was measured by a sensitive Dolezalek electrometer. A magnet placed near the Faraday chamber was sometimes used to turn back secondary electrons, for with fast rays they may cause a

great distortion of the curves. The resolution was sufficient to separate the first three constituents of the rays quite sharply but was not sufficient to distinguish with certainty between atomic weights of the ratio 6 to 7 or less. The first three parabolas are easily determined by their maxima coming at currents proportional to the square roots of the numbers.

The hydrogen which was prepared from zinc and hydrochloric acid could be allowed to stream from a reservoir into the tube through a fine capillary while the Gaede mercury pump was running; in this way pressure conditions could be kept constant. Liquid air was used on a U-tube to remove mercury and other vapors. An example of the curves obtained is given in Fig. 9. This curve was with 800-volt rays and a rather high pressure (about .01 mm.). H_1, H_2 and H_3 are present and other constituents which are probably O_1, O_2, O_2. The amount of H_3 obtained with these slow rays when the vacuum is not very high is apparently much greater than that obtained by J. J. Thomson by the usual method.

Effect of Decrease of Pressure.

One advantage of this method of producing the positive rays is that the rays may be made and examined in the highest vacuum. With the usual arrangement the vacuum in the analyzing chamber may be made high, but if the pressure in the discharge tube is much below .001 mm., the discharge refuses to pass or cracks the tube. With the present method the pressure may be varied over wide limits keeping the speed

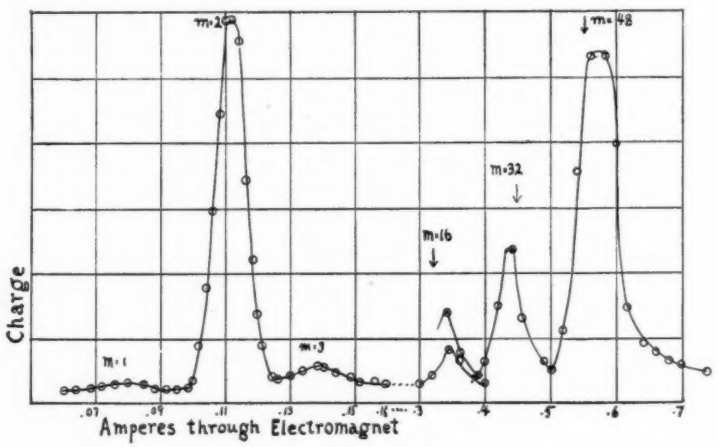


Fig. 10.

of the rays the same, and the change in the constituents of the rays examined as the pressure is altered. It was found that when the pressure was taken very low, using a charcoal bulb in liquid air connected to

both the discharge chamber and the analyzing chamber curves similar to that in Fig. 10 were obtained. The curve shown was obtained with 800-volt rays and the highest vacuum. Here the hydrogen atoms and H_3 are negligible in comparison with the hydrogen molecules. They regain, however, in relative intensity as the pressure is increased by admitting small amounts of hydrogen. At the low pressures, the free path is very large, so that the positive rays are analyzed in the condition in which they are just after being formed by the impact of the electrons from the Wehnelt cathode. The electrons thus ionize the gas merely by detaching a single elementary charge from the neutral molecule as concluded by Millikan[1] for ionization by β-rays and X-rays. The electrons cannot dissociate the molecules into atoms, but, when the pressure is taken higher so that the positive molecules make collisions, they dissociate the hydrogen.[2] That H_3 is not present when the gas is

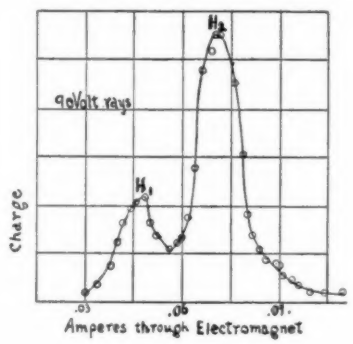


Fig. 11.

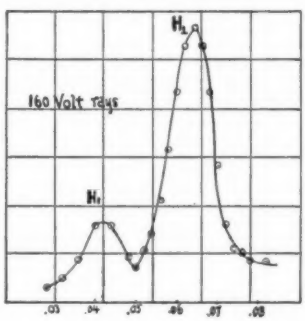


Fig. 12.

not dissociated shows that it is an unstable complex formed in the discharge tube itself, probably a neutral hydrogen molecule to which a charged hydrogen atom has attached itself. It is possible that with slow rays the formation of the complex is favored. There may also be an influence of impurities on the formation of H_3 at the higher pressures, but this matter and the change in the rays with the speed at constant pressure has still to be investigated.

The slowest rays thus far analyzed by the apparatus in Fig. 8 were with 90 volts between cathode and anode and at a pressure of hydrogen of about .0005 mm. Fig. 11 shows the two lightest constituents. The rays are diffuse and the pressure is so low that any H_3 is not apparent. Fig. 12 shows 160-volt rays under the same conditions of pressure.

My thanks are due to the members of the physics department and

[1] R. Millikan, Phil. Mag., 21, p. 753, 1911.

[2] J. J. Thomson, Phil. Mag., 24, p. 234, 1912.

especially to Professor Millikan for their readiness in assisting in every possible manner.

SUMMARY.

Positive rays excite light down to a speed less than that corresponding to a fall through 5 volts. They may be completely deflected by an electrostatic field.

Neutral rays in hydrogen excite light down to a speed corresponding to 50 volts. The theory that light is excited only during the return of a corpuscle to a positive center does not cover this case of light excitation.

The light caused by both the neutral and positive rays contains the hydrogen series lines.

Neutral rays of 800 volts speed change into positive.

Saturation curves are given for ionization by positive and neutral rays.

An apparatus for analyzing positive rays down to 90 volts' speed by the electric and magnetic deflection method is described.

At high vacua H_1 and H_3 are negligible in comparison with H_2, indicating that electrons ionize by detaching a single elementary charge from the neutral molecule, that the impact of positive rays is necessary for dissociation, and that H_3 is formed only when the gas is in a dissociated state.

RYERSON PHYSICAL LABORATORY,
UNIVERSITY OF CHICAGO.

A DIRECT READING PRECISION REFRACTOMETER WITH UNIFORMLY DIVIDED SCALE.

BY G. W. MOFFITT, PH.D.

I. INTRODUCTION.

WHILE reading some articles on the use of a lens and a plate of glass to determine the indices of refraction of liquids it occurred to me that an optical system might be devised in which the change in position of the image of a point source would vary directly with the index of refraction of the liquid between the plane and the curved glass surfaces. No description of such a system could be found in any of the texts and journals available, but a little work with the well-known equations of conjugate focal relations at refracting surfaces led to the desired formula. Since no description of a similar type of instrument was found, and since the instrument possesses many good points, a brief description of it is here given.

The advantages of the instrument are simplicity, ease of operation, linearity and openness of scale, and a sensitiveness comparing with that of the total reflection instruments. The entire operation of determining the refractive index of a liquid consists in placing a drop of the liquid at the proper place on a convex surface, bringing the nose of the microscope down upon it, and focusing the eye-piece. The value of the index is then read off directly from the uniformly divided scale on the focusing tube of the instrument. In an instrument of convenient size the change in setting for a change in index from 1.000 to 1.500 may be as much as ten centimeters. With an eye-piece of fairly high power the uncertainty in a setting need not be more than 0.02 cm. In most cases it will be less. The sensitiveness will, therefore, compare favorably with that of the best total reflection instruments.

II. THEORY.

Case 1.—Consider the arrangement shown in Fig. 1. Let a point source of light be placed at C, distant R below the surface of the liquid. Its image due to the refraction at the surface of the liquid will be at S, so that $ST = R/n$, where n is the index of refraction of the liquid. Let S act as a virtual object at distance $k + R/n$ from a converging lens L

of focus f, and let the image of S formed by this lens be at I, distant p from the lens. Then

$$\frac{1}{k + R/n} + \frac{1}{p} = \frac{1}{f}. \tag{1}$$

Clearing of fractions,

$$npf + knf + Rf = pkn + Rp. \tag{2}$$

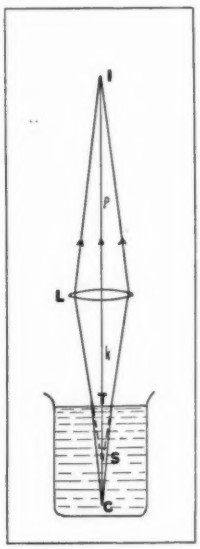


Fig. 1.

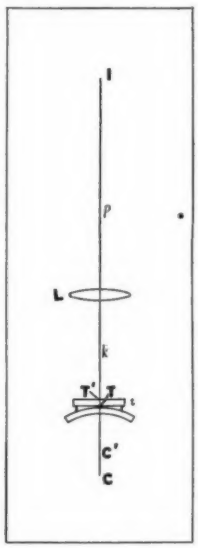


Fig. 2.

This equation becomes linear in n and p when

$$npf = npk, \quad \text{or when } k = f. \tag{3}$$

Equation (2) then becomes

$$n = \frac{R}{f^2}p - \frac{R}{f}. \tag{4}$$

That is, if equation (3) is satisfied the position of the image depends directly on the index of the liquid.

Case 2.—Consider the arrangement shown in Fig. 2. Let the point source be placed at C, the center of curvature of a spherical lens having concentric surfaces, and let a drop of the liquid be placed between the lens and a plane parallel glass plate placed in contact with the lens. The treatment differs from that of Case 1 in that the effect of the plane parallel glass plate must be considered. Beginning with C as a point source to locate its image C' by refraction at the surface T we have the following equation:

$$C'T = \frac{Rn'}{n}, \tag{5}$$

where n' is the index of refraction of the plane parallel plate. In the same way the refraction at T' may be expressed.

$$ST' = (C'T + t)\frac{1}{n'} = \frac{R}{n} + \frac{t}{n'}, \tag{6}$$

where t is the thickness of the plane parallel glass plate. From the equation of the converging lens,

$$\frac{1}{p} + \frac{1}{\frac{R}{n} + \frac{t}{n'} + k} = \frac{1}{f}. \tag{7}$$

The condition that this equation be linear in n and p is

$$\frac{t}{n'} + k = f. \tag{8}$$

Making this substitution and clearing of fractions we have

$$n = \frac{R}{f^2}p - \frac{R}{f}. \tag{9}$$

It will be noticed that equation (9) is identical with equation (4), but that the conditions for linearity of scale stated in equations (3) and (8) are slightly different owing to the effect of the plane parallel glass plate. It will be seen that in both cases the adjustment for linearity of scale is such that if parallel rays were incident upon the upper face of the lens L they would be brought to a focus at the plane surface of the liquid.

Case 3.—Consider the case when the source is not at the center of curvature of the concentric lens, or when the lens is of some other form, but at a distance from it such that its apparent distance from the curved liquid surface is u. The image by refraction of the liquid lens into the plane parallel plate is according to the equation for the plano-concave lens bounded on the plane side by a medium of index n'.

$$\frac{n'}{C'T} - \frac{1}{u} = \frac{n-1}{R}, \quad \text{or} \quad C'T = \frac{uRn'}{R + u(n-1)}. \tag{10}$$

The refraction at T' may be expressed as follows:

$$ST' = \frac{C'T + t}{n'} = \frac{uR}{R + u(n-1)} + \frac{t}{n'}. \tag{11}$$

The object distance for lens L is

$$SO = \frac{uR}{R + u(n-1)} + \frac{t}{n'} + k. \tag{12}$$

Applying the equation for the converging lens,

$$\frac{1}{p} + \frac{1}{\dfrac{uR}{R + u(n-1)} + \dfrac{t}{n'} + k} = \frac{1}{f}. \tag{13}$$

Differentiating with respect to n,

$$\frac{dp}{dn} = \frac{u^2 R n'^2 f^2}{\{uRn' + (t + n'k - n'f)[R + u(n-1)]\}^2}. \tag{14}$$

When the condition expressed in equation (8) holds

$$t + n'k - n'f = 0, \tag{15}$$

and the slope is a constant, equation (13) taking the simpler form

$$n = \frac{R}{f^2} p + \left(1 - \frac{R}{u} - \frac{R}{f}\right). \tag{16}$$

When k is too large the second term in the denominator is positive and increases with n. Therefore the slope decreases as n becomes greater and the curve is concave toward the axis of n. If k is too small the reverse is true and the curve is concave towards the axis of p. If u be set equal to R equation (16) becomes identical with equation (9), that equation being a special case of the general equation just derived.

Relations Between Dimensions of Object and Image.—Let C represent the size of the object in Fig. 2, and let C', S and I represent the size of the images formed at these respective points. Then

$$\frac{C'}{C} = \frac{C'T}{u} = \frac{S}{C}, \tag{17}$$

since no change in size of image is produced by the refraction at T'. By refraction at the converging lens L,

$$\frac{I}{S} = \frac{p}{SO}. \tag{18}$$

Combining (17) and (18),

$$\frac{I}{C} = \frac{S}{C} \times \frac{I}{S} = \frac{C'T}{u} \times \frac{p}{SO}. \tag{19}$$

Substituting the values of $C'T$, p, and SO from equations (10), (12), and (16), and simplifying,

$$\frac{I}{C} = \frac{f}{u}. \tag{20}$$

The image is of constant size for a fixed value of u, a property of the system utilized in a method for precise focusing to be described in a later paragraph.

III. ABERRATIONS.

Spherical Aberration and Distortion.—With the direct illumination that may be used in this instrument it is possible to use a stop of rather small diameter and still have a well-lighted field of view. Since only a small portion of each lens is used in forming the image of any point in the object the effect of spherical aberration in blurring the image is very small. Therefore it seems unnecessary to take particular precautions to eliminate spherical aberration.

Curvature of the image, however, may affect the performance of the instrument to a slight extent. The curvature of the virtual image formed by the liquid lens is concave towards the eye-piece. The effect of the converging lens L in forming the image at the eye-piece is to diminish the curvature. The curvatures of the surfaces and the position of the stop should be so chosen that the resulting image will be as nearly plane as possible over the area covered by the image at the eye-piece.

Even if the radius of curvature of the image were as small as 5 cm. in an instrument whose image were 0.5 cm. in extent the periphery of the image would be out of the plane of the center by

$$h = \frac{d^2}{8R} = \frac{25}{400} = 0.06 \text{ mm.}$$

This value is less than the error of a setting. And since the focusing is always done on the peripheral portions of the image the effect would be to change slightly the position of the zero point of the scale.

Chromatic Aberration.—In considering the chromatic properties of the system two distinct cases arise. If the converging lens L be strictly achromatic the adjustment for k is correct for all wave-lengths. The instrument will not give an achromatic image at the eye-piece, but the various colored images will be distributed along the axis according to the dispersion of the particular liquid in the apparatus. Such should be the construction of the refractometer if it is desired to measure the value of the index for different wave-lengths in order to determine the dispersion of the liquid. In this case monochromatic illumination is of course necessary. Lens L must be thoroughly achromatized in order that the adjustment of k shall be correct for all the values of wave-length with which the instrument is to be used.

The other case arises when the lens L is of the simple uncorrected type. This leads to a construction which may be approximately achromatized for liquids of ordinary dispersion, and which when illuminated with white light will give the index for some particular value of the wave-length for which the instrument has been calculated. Considering the

positions of the red and the blue images formed by the liquid alone, we find that the blue image lies nearer the lens L than does the red image. If the chromatic properties of this lens are such that its images of the images formed by the liquid lens fall at the same point the system will be achromatic in the sense that the different colored images will be at the same point in the eye-piece. This condition can be realized only for liquids whose dispersion bears a certain relation to the index of refraction for some intermediate wave-length. Since no such relation is general it will be seen that it is not possible to completely achromatize the instrument although an approximation may be realized which will be satisfactory for many liquids. Whenever it is desired to use the instrument with a liquid which gives chromatic effects detrimental to accurate focusing it would be necessary to use the monochromatic light for which the instrument was designed to give accurate readings.

The condition for approximate achromatization may be derived as follows. For the convergent lens L, assumed bi-convex,

$$\frac{1}{V_F'} - \frac{1}{V_C'} = \frac{V_C' - V_F'}{V_C' V_F'} = \frac{V_C' - V_F'}{V_D'^2} = \frac{2d'}{r}, \tag{21}$$

where V_F' and V_C' are the virtual object distances for the lens L for the same value of p, and where $d' = n_F' - n_C'$ for the lens, and r is the radius of curvature of the lens faces. For the plano-concave liquid lens,

$$\frac{V_C - V_F}{V_F V_C} = \frac{V_C - V_F}{V_D^2} = \frac{d}{R}, \tag{22}$$

where V_C and V_F are the distances from the liquid to the corresponding images for a given value of u. R is the radius of curvature for the curved surface of the liquid and $d = n_F - n_C$. The condition for achromatization is

$$V_C - V_F = V_C' - V_F'. \tag{23}$$

Dividing (21) by (22) and substituting (23),

$$\frac{V_D^2}{V_D'^2} = \frac{2Rd'}{rd}. \tag{24}$$

This reduces to

$$uR\sqrt{2f_D(n_D' - 1)d} = n_D f_D u\sqrt{2Rd'} + (uR + f_D R - f_D u)\sqrt{2Rd'}, \tag{25}$$

which shows that it is possible to achromatize the system for any liquid whose mean index bears a certain relation to the square root of its dispersion. This relation is determined by the constants of the optical system.

IV. The Instrument.

The refractometer may be set up in a convenient form resembling an ordinary microscope in appearance. Instead of the usual stage a heating tank may be provided, through the center of which passes a spring mounted tube carrying the object scale at the lower end and the lens on which the liquid is placed at the upper end. The spring mounting lifts this tube so that the lens comes above the top of the heating jacket when the microscope is raised. In this position it is easy of access for cleaning and for placing the drop of liquid in position. At the lower end of the microscope tube is placed the plane parallel plate, and up in the tube at the proper distance is placed the converging lens L. The microscope tube is arranged so that it may be lowered into position and the two lenses brought into contact, and in contact with the liquid, and lowered into the heating jacket. The eye-piece should be mounted in the end of a tube telescoping into the microscope tube with rack and pinion adjustment for ease of focusing. The focusing tube should also be provided with a scale, read with a vernier, whose divisions are in accord with equation (16) if the instrument is to be direct reading. The eye-piece should be of fairly high power and should be mounted in such a manner that it and the eye-piece scale may be moved laterally a short distance in order to enable the user to bring the image and the scale into coincidence.

Adjustments.—The adjustments of the instrument are few and simple. The converging lens and the plane parallel plate must be carefully fixed with respect to each other. On this adjustment depends the linearity of scale. It will be seen that the proper adjustment is such that parallel light incident on the lens from above is brought to a focus on the lower surface of the plate. If the system be lined up with a telescope focused for parallel light by the auto-collimation method, the adjustment may be made by eliminating parallax between the cross wire of the telescope, and the images of fine dust particles on the lower surface of the plate. If the lens is not achromatic this adjustment should be made with monochromatic light of the same wave-length for which the instrument is to read correctly.

Focusing.—In the development of the equations it was shown that the image in the eye-piece is of a fixed size whenever the instrument is in proper focus. The ratio of the image size to the object size is given in equation (20). Therefore if two scales be ruled with divisions in the ratio of f to u the one may be used as an eye-piece scale and the other as an object whose image is formed at the eye-piece. When focusing is complete image and eye-piece scale will be of the same size and coincident.

Position of Stops. Effect on Focusing.—The rays usually used when locating the position of an image graphically are seldom those that actually form the image. The position of the stop that limits the aperture of the instrument determines the rays that actually form each part of the image. This would seem to be of small importance here in its effect on spherical aberration and curvature of field but it plays an important part in focusing by comparison of image with eye-piece scale. While the eye-piece is moved outward throughout the range of clear focus we may have the image increasing, decreasing, or remaining of constant size, depending on the position of the stop. And the steeper the slope of the chief image rays with the axis of the instrument the greater will be the accuracy with which the focusing may be done. Several cases arise.

1. When the stop is between the object and the liquid lens the chief image rays are slightly convergent and the image increases in size as the eye-piece is racked in. This convergence is never very great. A rather large aperture for the liquid lens is also required. For these reasons this position of the stop is not good.

2. When the stop is in the plane of the liquid lens it is at the principal focus of the lens L and the chief image rays are parallel. No change in the size of the image results on moving the eye-piece toward or away from the lens. Accurate focusing cannot be done with the stop in this position.

3. When the stop is at the converging lens the chief image rays diverge from a point approximately coincident with the optical center of the lens. Their slope decreases with increase of the index of the liquid, thus decreasing the accuracy of a setting for the higher values of the index. It is apparent, however, that the decrease in accuracy is less rapid than the increase in value of the index so that the percentage error decreases with increase of the index. It will be noted that the center of the liquid lens is used to form the center of the image while the peripheral rays form the edge of the image. This arrangement enables one to focus with a good degree of precision.

4. If the stop be placed at a fixed distance above the converging lens, say at its principal focus, the divergence of the chief image rays is increased over that of Case 3, and the accuracy of a setting thereby increased. Between the liquid lens and the converging lens the chief rays are parallel to the principal axis. The effective apertures of both lenses are the same and vary inversely with the index of the liquid. The percentage accuracy of the settings is a constant because the distance from the stop to the image is directly proportional to the index of the liquid. This position of the stop seems most likely to give high precision

in the readings. Evidently the most accurate settings can be made when the divergence of the chief image rays is as great as is consistent with a good length of image and reasonably small apertures of the lenses, especially of the liquid lens. Since the aperture of the lenses is increased by bringing the stop nearer the eye-piece it is seen that there is a limit where the increase in aberration effects due to increased aperture of the lenses will counterbalance any gain in accuracy of focusing due to increased divergence of the chief image rays.

A compact instrument with a very open scale, and covering a long range, might be constructed in the following manner. Let the spring mounted tube carry three object scales instead of one. Let these scales be so ruled and placed that when focusing on the first scale values of index from 1.000 to 1.2 + would cover the range of the engraved scale of the instrument. By focusing on the second scale values from 1.2 to 1.4 + could be read, and by focusing on the third scale values from 1.4 to 1.6 + could be determined. Such an instrument would be of practically the same size as one with single scale covering the same range with one third the openness of scale. With certain values of index two scales would be in focus in the field of view at the same time. Each scale should be given a distinguishing mark and the three should be placed at different angles across the field of view in order to prevent confusion of the scales.

V. Experimental.

After considerable preliminary work a single scale instrument was constructed essentially as described above. The lenses, except the optical flat, were made by a local firm of spectacle lens grinders. The centering was not all that could be desired and for this reason a satisfactory study of the effect of varying the position of the stop was impossible. The stop was placed at the converging lens L which had a focal length of about 8.5 cm. The aperture used was somewhat less than a centimeter in diameter. The radius of curvature of the upper face of the concentric lens was 6.0 + cm. Actual openness of scale was found to be 1.282 cm. for a change of 0.1 in the index of the liquid. The value of u was placed equal to that of f, since that adjustment leads to the shortest tube length for the instrument. It also leads to more accurate focusing than when the tube is longer since the chief image rays are more divergent. The length of the object and the image scales was 0.5 cm. The approximate adjustment of k was made by the collimation method already described using sodium light.

Careful determinations of the index of refraction were then made for several liquids using a spectrometer and a hollow 60° prism. Imme-

diately after the deviation readings were taken with the spectrometer a drop of the liquid was removed from the prism and placed in the refractometer. A number of settings were made and the reading of the centimeter scale on the focusing tube of the instrument recorded each time. This procedure was carried out for all the liquids in the table below.

Substance.	Spectrometer Value of n.	Refractometer Readings.
Air	1.0000 (assumed)	1.42 cm.
		1.41
		1.42
		1.41+
Water	1.3318	5.57
		5.59
		5.58
Kerosene	1.4475	7.02
		7.03
		7.04
Cedar oil	1.4994	7.63
		7.66
		7.67
Carbon bisulphide	1.6209	9.12
		9.14

Curve I., Fig. 3, shows these results graphically. It will be noticed that the curve deviates somewhat from a straight line, being concave

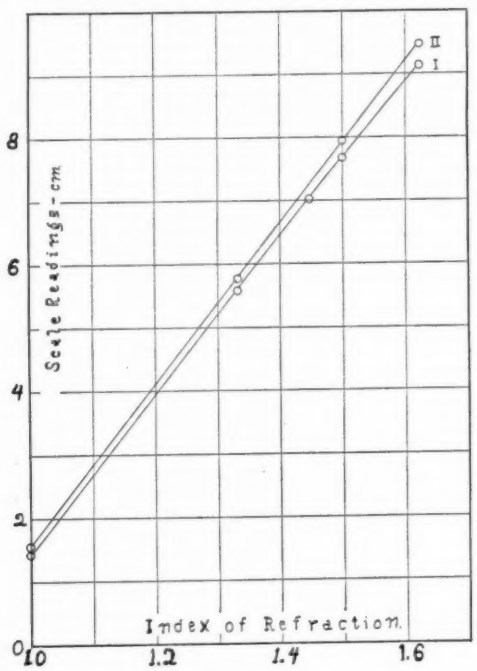


Fig. 3.

towards the axis of index of refraction. If we refer to equation 14, which gives the slope of this graph as n varies, we see that the curve would be concave toward the axis of indices when the value of k is too great.

The value of k was then decreased by 0.03 cm. and readings again taken. The results are shown in Curve II., Fig. 3. The graph is sensibly a straight line.

The illumination for all the readings was furnished by a Bunsen burner whose flame was colored by a piece of asbestos soaked in a solution of common salt.

The work shown here is no better than should be done in general with an instrument properly scaled, adjusted and centered.

VI. Summary.

The simple direct reading refractometer constructed according to the equations derived in this paper possesses the following qualities which are very desirable in such an instrument.

1. A linear scale calibrated directly in terms of the index of refraction of the liquid under examination.

2. The possibility of so constructing the instrument that white light may be used when it is desired to determine the mean index, the instrument still retaining approximate achromatization in many cases.

3. Simplicity and ease of manipulation.

4. Few adjustments other than those fixed permanently in the construction of the instrument.

5. Settings obtained by comparing the dimensions of an image with those of an eye-piece scale, an accurate means of adjustment.

6. Adequate means for temperature control whenever required.

7. Ability to determine the index to one or two points in the third decimal place.

Washington University,
May, 1916.

ON A MODIFICATION OF THE HILGER SECTOR PHOTOMETER METHOD FOR MEASURING ULTRA-VIOLET ABSORPTION AND ITS APPLICATION IN THE CASE OF CERTAIN DERIVATIVES OF FLUORAN.

By H. E. Howe.

COLOR in chemical compounds, or the lack of it, has been made the basis for decisions regarding the molecular structure of the compounds. Since color depends upon the absorption of light in the visible part of the spectrum only, it would seem that ultimate conclusions as to the relation between structure and absorption will necessitate a knowledge of the complete absorption spectrum from ultra-violet to infra-red.

The work described was begun for the purpose of studying the effect on the ultra-violet absorption of a group of related phthaleins when halogen or hydroxyl groups are substituted for hydrogen in the molecule and of determining what change in the absorption spectrum occurs when colorless alcoholic solutions of these phthaleins become colored upon the addition of alkali. The absorption curves presented in this paper are too few to form a basis for general conclusions, but they serve to illustrate the method of work.

In connection with the work of determining the ultra-violet absorption of the solutions studied, two physical problems were met. These were (1) the establishment of a method by which measurements can be made with the Hilger sector photometer and (2) the development of a source of light satisfactory for use in the ultra-violet. The author has found that the photographic plate, the use of which in photometric measurements is usually considered questionable, integrates intermittent exposures in such a way that the comparison of two intensities can be made directly in terms of sector openings provided that the time from the beginning to the end of the exposures is the same and that the two exposures produce equal blackenings of the plate. The aluminum spark under water, described by Henri,[1] has been improved until it has become a very strong source, easy of control and reasonably constant. The spectrum which this source gives is continuous with only a few lines superposed and can be used, with long exposures, to .21 μ.

[1] V. Henri, Phys. Zeit., 14, p. 516, 1913.

THE MANIPULATIVE PROBLEM.

In plotting absorption curves a method proposed by Baly and Detsch[1] has been followed by chemists almost without exception. Photographs of the spectrum of the light source and of the transmission spectra of layers of different thickness are taken on the same negative, the same time of exposure being used throughout. The "limits of absorption," *i. e.*, the points where the transmission spectrum has blackened the plate the same as the unmodified spectrum, are marked on each photograph, and these limits are plotted against the relative thicknesses of the most dilute solution used.

The great difficulty of this method lies in the determination of the limits of absorption, because the two parts of the plate being compared are so far apart. This difficulty, which is especially noticeable if the source used gives a line spectrum, is illustrated in Plate I. The upper photograph was made using an iron spark and a solution of anthracene in alcohol, with thicknesses from 1 mm. to 50 mm. One is inclined to mistake for absorption bands what are really weak places in the spectrum of the source.

The second photograph was made in the same manner as the first, except that the aluminum spark under water was used. The superiority of the second source is apparent. But with either source there is still an objection to the method, for no allowance is made for the absorption of the solvent, and the error is a varying one as the thickness of the

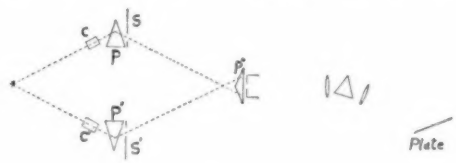


Fig. 1.

absorbing layer changes. With alcohol as a solvent the error in the extreme ultra-violet is considerable. Curves plotted from either of the two negatives here reproduced show a much greater absorption in the short wave-lengths than does the true curve for the solute alone.

The third photograph in Plate I. is from a negative made with the apparatus to be described. From such a negative the true absorption of the solute can be found.

The arrangement of the parts of this apparatus is shown in Fig. 1, which for convenience is made to show the spectrograph in plan and the photometer attachment in elevation. Two beams from the source pass

[1] Baly and Detsch, Trans. Chem. Soc., 85, p. 1039, 1904.

through the quartz prisms P and P', and when incident on the small biprism P'', are so bent that they are focused by the spectrograph as two narrow spectra with a fine dividing line between. The sector S' has a constant opening of 180°. S is variable and has a scale reading in logarithms of the relative openings of S' and S. The absorbing solution is put into the cell at C' and a similar cell, filled with the solvent, is placed at C. Exposures through the two cells are made simultaneously. Sixteen exposures are made on one negative, with sector scale readings from 0 to 1.5.

On the developed negative the points of equal blackening are marked and the corresponding frequencies read by means of a transparent frequency scale. To locate the points of equal blackening the negative is laid on an illuminated milk glass plate and a paper screen with a small hole in it is moved along the blackened strip until the point of match is found. A dot is then made with a fine pen. In this way a sort of curve is "spotted" on the negative. The "spotted" negative is then laid over the frequency scale and the frequency of each point of match read. The scale used was made by photographing to proper size a magnified scale drawn from the calibration curve of the spectrograph. The known frequencies of the aluminum lines showing on the negative enables one to place the scale properly under the negative to be examined.

Attempts to read the points of equal blackening by the use of (1) a micrometer microscope and (2) a projection lantern with a cross-hair moving over the negative showed that the spotting method was quicker, easier on the eyes, and quite as accurate.

Great care must be taken to keep the alignment of the apparatus correct. The light must come from a narrow horizontal source (a spark between metal electrodes was used), and a very small displacement of the line source up or down causes inequality of the two beams reaching the plate. When such a displacement occurs, the fact shows up in a test photograph by one of the blackened strips being darker at one end than is the other strip, while at the other end, the inequality is reversed. Thus the error is least in the middle part of the spectrum (between frequencies 3,000 and 4,000). It is in this part of the spectrum that most of the readings reported were taken. As a precaution, the first and last exposures on each negative were made with both cells C and C' removed. If the electrodes had become displaced, the negative was discarded.

Calling I and I' the intensities of the beams transmitted by the two cells C and C', the ratio I/I' represents the ratio of intensities of a beam of light before and after its passage through a layer of the dissolved substance, considered alone. If this layer of absorbing molecules is of

thickness d and concentration c (gram-molecules per liter), we may write

$$\frac{I}{I'} = 10^{\beta cd} \quad \text{or} \quad \beta = \frac{1}{cd} \times \text{Log} \frac{I}{I'}$$

β is called the "molecular absorption constant" (or sometimes, "molecular extinction coefficient"). This relation assumes that the dilution is such that the relative number of active molecules is independent of the concentration, *i. e.*, that Beer's law is followed.

Suppose a photograph taken with S set at .3, *i. e.*,

$$\text{L g} \frac{\text{opening } S'}{\text{opening } S} = .3,$$

and that the spectra obtained cause equal blackening for some wave-length. If the photographic plate integrates the incident energy properly, we can say

$$\text{Log} \frac{\text{light incident on absorbent}}{\text{light transmitted by absorbent}} = .3 = \text{Log} \frac{I}{I'}.$$

Reasons for assuming this relation to hold will be discussed in the following paragraphs.

THE PHOTOGRAPHIC PROBLEM.

In photometry by photographic means one may use the Schwarzschild[1] relation, $I_1 t_1^{\delta} = I_2 t_2^{\delta}$, when the two regions of the plate to which the I's and t's apply are blackened equally by continuous exposures. The exponent δ depends upon the brand of plate. Its possible variation with the handling of the plate during exposure and development, and the possible growth and decay of the latent image after exposure make the application of the relation somewhat questionable.

The only relation that will unquestionably apply was stated by Hartmann somewhat as follows: two beams of light which produce equal blackening of two areas of the plate may be taken as equal provided (1) the two beams are of the same wave-length; (2) they act upon closely adjacent parts of the plate; (3) they are of constant intensity, or vary together; (4) they act simultaneously. These conditions are imposed because (1) the sensibility of the plate varies with the quality of the light, (2) the plate may vary from point to point, (3) and (4) the relation between I, t, and the blackening is uncertain.

All of these conditions except the fourth are met by the Hilger apparatus. The total time from the beginning to the end of exposure is the same for the two beams. But the beams are of unequal intensities, and the actual times during which they act on the plate are unequal,

[1] Schwarzschild, Astr. Jour., 11, p. 89, 1900.

being inversely proportional to the sector openings. Hence it becomes necessary to determine, for each ratio of sector openings, what relative intensities will produce equal blackenings under the conditions stated.

The writer has found that the intensities are inversely proportional to the sector openings, *i. e.*, $I/I' \propto S'/S$. The makers of the apparatus assume no such simple relation and propose an experimental determination of the relation for each brand of plate used. The relation is assumed to be similar to the Schwarzschild relation. The makers supply with the photometer a thin glass plate and a curve showing its Log I/I' for all frequencies. This plate was placed in front of the 180° sector and a series of exposures made with the upper sector varied. On the completed negative the frequency of the points of equal blackening were read. The maker's curve supposedly gave Log I/I' and the scale reading gave Log S'/S. A curve drawn with these two quantities was supposed to be the calibration curve of the sector apparatus for the brand of plate used. Log I/I' was called the "effective absorption constant" of the sector apparatus for the sector ratio S'/S.

The application of the resulting curve to the writer's data on absorption gave different values for β when the concentration or the thickness of the absorbing layer was changed. But β can not depend on the thickness, and for the concentrations used ($N/5{,}000$ or less) Beer's law could be expected to hold. The results indicated that the absorption curve furnished with the glass plate was incorrect.

It was therefore necessary to determine the nature of the sector correction by some other method. Five nearly neutral smoke-glass plates were cut to fit the sector apparatus. The transmission of these plates, which was sensibly uniform in the yellow-green part of the spectrum, was carefully determined at $\lambda = .546\ \mu$ on a spectrophotometer. Each plate was then placed in front of the sector S of the photometer apparatus, and with both sectors running the setting of S' that gave the best match in the green was determined several times. The photographic plates used were sensitive for a small region on both sides of $.546\ \mu$. To get greater values of Log I/I' two plates were superposed, care being taken that they were not in contact. In such a case, Log I/I' for the combination equals the sum of the separate values within a negligible error.

Fig. 2 shows the relation between Log I/I' (determined visually) and Log S'/S (determined photographically). The visual values are averages of 20 to 30 readings, while three or four determinations were made of each photographic value. The circles show Log S'/S with the lower sector running, and the crosses show Log $360°/S$ with the lower sector at

rest. The fact that the points lie on a straight line whose slope is unity shows that $I/I' = S'/S$.

As a further test of the relation, absorption photographs were made as described, using two thin glass plates over the lower sector opening, first separately and then superposed. Fig. 3 shows the curves obtained.

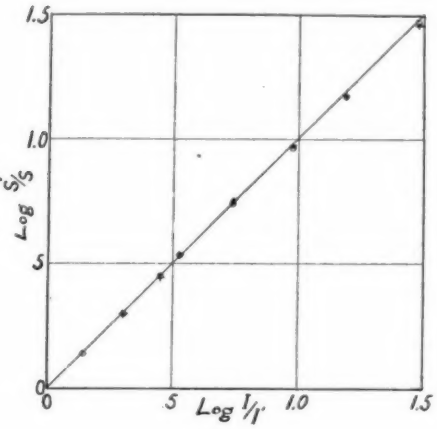


Fig. 2.

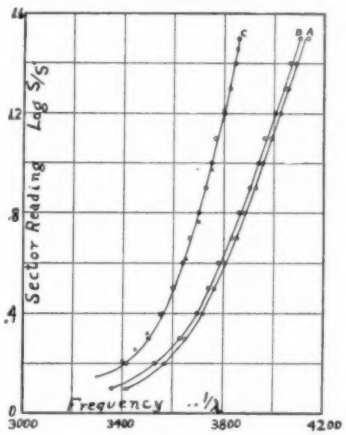


Fig. 3.

A, glass plate No. 1; *B*, glass plate No. 2; *C*, plates 1 and 2 superposed.

The sum of the ordinates of the two lower curves (indicated by crosses) equals the ordinate of the upper curve for any frequency. This agreement indicates that $I/I' = S'/S$.

Stopping the lower sector in front of which the thin glass plate was placed and making a series of exposures with the upper sector varied, a curve was obtained with sector scale readings just .3 less than with the lower sector running. .3 is log 2. Thus, S'/S remains the same, whether S' is 180° or 360°. The significance is that two beams can be compared by cutting down one of them with a rotating sector until a photographic match is obtained, the reading of the sector being used directly.

Fig. 5 (for fluoran) shows that different concentrations give constant β's for any wave-length, if we assume $I/I' = S'/S$. A similar assumption checks with the curve for β-orcinolphthalein (Fig. 8), which gives β independent of thickness.

EFFECT OF EMULSION.

If the comparison of light intensities photographically when rotating sectors are used depends upon a relation of the Schwarzschild form, different emulsions should give different values of Log S'/S for a constant Log I/I'. To investigate this possibility, the thin glass plate previously

mentioned was used in the making of negatives with Seed's Ortho C plates two years old (two negatives), the same brand four months old (five negatives), the same with a fresh emulsion (four negatives), and a special "even sensitiveness" plate from the Eastman laboratory (two negatives). All the plates gave practically the same curve.

In only one case (Fig. 2) has it been certainly proved that $I/I' = S'/S$. The other experimental results might be explained on the assumption of proportionality of I/I' and S'/S, and the factor of proportionality might be different for different wave-lengths. However, this factor would reasonably be expected to depend upon the sector opening and brand of plate, if upon anything. The evidence seems to the writer sufficient to justify the assumption of equality.

A similar conclusion has been reached by Weber,[1] from results obtained in an entirely different manner and which seem to prove the proportionality of I/I' and S'/S. In Weber's work a continuous exposure was matched against an exposure through a rotating sector. Upon cutting down the first exposure half by a geometrical screen, the sector opening that gave a match was found to be half that in the first case. This result was determined at six different wave-lengths and with several brands of plates.

The "characteristic curve" for a photographic plate, as usually plotted, gives the "density" of the plate plotted against the logarithm of the time of exposure to a source of constant intensity. Two curves which would throw light on the conclusions of this paper, and which the writer has not been able to find published, are (1) a curve in which density is plotted against the varying intensity to which the plate is exposed for equal times, and (2) a curve in which density is plotted against the openings of a sector through which exposures are made for equal times. The curves would seemingly be similar in form. It is proposed to obtain them in verification of the conclusions as to the use of a rotating sector.

The general impression of the unreliability in the use of the photographic plate for photometric work has arisen undoubtedly from the fact that in the earlier work the attempt was made to compare intensities by comparing the unequal blackenings of the plate when both the intensities and the times were different. This could not be done simply. Further confusion arose from the attempt to compare different negatives.

The above considerations as to the applicability of the photographic plate may be represented concisely in the table below, which shows three ways in which a definite amount of energy may act upon a photographic plate.

[1] A. E. Weber, Ann. der Physik, 45, p. 801, 1914.

Intensity.	Total Time of Exposure.	Manner.	Effective Time.	Blackening.
I.....	t/n	Continuous	t/n	B_1
I/n.....	t	Continuous	t	B_2
I.....	t	Intermittent	t/n	B_3

The second case may be realized by interposing an absorbing screen that transmits only $1/n$ of the light. The third case is that of a rotating sector whose angular opening is $360°/n$. It is known that B_1 is greater than B_2 (Schwarzschild relation), and that B_1 is greater than B_3 (Abney[1]). The human eye judges the third intensity to equal the second. The results of the work discussed above show that the photographic plate integrates the third exposure in such a way as to give B_2 equal to B_3. The absorption curves are plotted on this assumption.

THE SOURCE OF LIGHT.

The arrangement of the electrical circuit for the production of a spark between aluminum electrodes under water is shown in Fig. 4. T is an

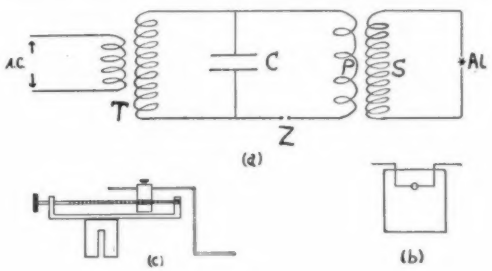


Fig. 4.

oil transformer of the closed magnetic circuit type, joined through resistance to the 110-volt A.C. mains. The capacity C consists of nine Leyden jars, each with a capacity of about .002 mf. P and S represent a Tesla transformer. The primary has four turns of heavy wire forming a coil 45 cm. in diameter, which is placed around the center of the secondary. The secondary consists of a single layer of annunciator wire wound on a wooden frame 60 cm. long and 30 cm. in diameter. A spark gap is at Z. High frequency oscillations are set up in the Tesla circuit and the discharge occurs at the gap Al, under distilled water.

Fig. 4 (b) shows the arrangement of the aluminum electrodes behind a quartz window that is cemented over a hole in the side of the battery jar used to contain the distilled water, and Fig. 4 (c) indicates the way in which the electrodes are attached and made movable. Aluminum rods 2 mm. in diameter were used.

[1] Abney, Jour. of Phot. Soc., 1893–4.

The aluminum spark is affected greatly by the action of the spark at *Z*. Several sorts of spark gap were tried. The best form consisted of two zinc discs cast on steel shafts and so mounted as to rotate with their edges about 3 mm. apart. This arrangement gave a spark which was fairly uniform in action and which never failed to start when the circuit was closed. With it, a very uniform aluminum spark about 5 mm. long could be maintained. The slight variations still evident seemed due to heating of the discs.

A small amount of tap water sufficed to render the discharge between the aluminum electrodes silent, an effect due supposedly to the increased conductivity. The collection of impurities from the air or to some chemical action produced by the spark necessitated a change of the water in the jar about once a week.

Nickel, iron, and aluminum, used as electrodes for a spark in air, all give spectra rich in ultra-violet lines, nickel being strongest in the extreme ultra-violet. Placing the electrodes under water cuts down the intensity of the extreme ultra-violet but gives a continuous background which seems to be independent of the metals used. Aluminum gives fewer lines superposed on the continuous background than either of the other metals and is therefore better. Much of the time the only lines that are easily noticeable are the two strong pairs at .396–.394 μ and .309–.3075 μ. These pairs serve as landmarks when the frequency scale is laid on the negative.

The condenser circuit requires rough tuning, the intensity of the spark being increased as resonance is approached. The substitution of inductance for capacity in the Tesla primary circuit decreases the intensity without modifying the character of the spectrum. The zinc gap could be varied from 2 mm. to 7 mm. with a resulting increase in brightness of the source, and the aluminum spark gap could be varied from 2 mm. to 10 mm., the longer spark being most nearly free from lines. For smoothness and certainty of action the gaps were used with lengths of about 3 mm. and 5 mm. respectively.

The bubbles of gas formed as the water decomposes under the action of the spark are thrown violently in all directions. Often they wander back into the spark and disappear. The mechanical effect of the spark is also seen in the disintegration of the aluminum rods, which look as if battered with a hammer.

The source obtained with the above arrangement is so bright that in photographing with the Hilger instrument with the spectrograph slit .05 mm. wide the time of exposure for a considerable part of the spectrum need not be more than 10 seconds. The table below shows the relative

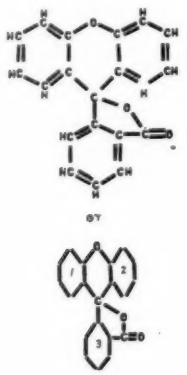
times necessary to cause equal blackenings on the Seed's Ortho C plate used by the writer. Most of the work was done between .50 μ and .24 μ, where the blackening was most uniform.

Wave-lengths.	Relative Exposures.
.50–.46 μ	2
.46–.33	1
.33–.28	1.5
.28–.25	2
.25–.24	3
.24–.23	5
.23–.22	10
.22–.21	20

Discussion of the Absorption Curves.

The substances studied were chosen because they form a related group of which new compounds were being prepared in the laboratory of chemistry. Unless otherwise stated the solutions used were colorless solutions in neutral absolute alcohol. Some of the solutions become colored upon the addition of KOH. The corresponding change in the ultra-violet absorption has been investigated in some cases and will be the subject of further study by the author.

The graphic formula for each compound is shown in connection with its curve of absorption. The benzene ring, C_6H_6, is represented by a hexagon (Fig. 5), the sides of which represent chemical bonds. At each



Flouran

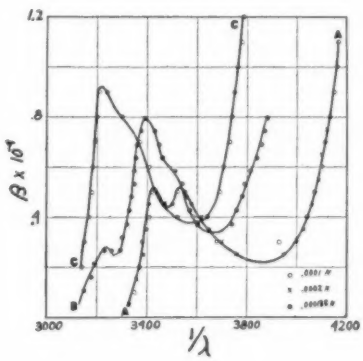


Fig. 5.

A, fluoran; *B*, tetrachlorofluoran; *C*, tetrabromotetrachlorofluoran.

corner of the hexagon is placed a C atom with its attached H atom. These H atoms may be replaced by halogen, hydroxyl, or methyl groups, etc. In the graphic formulas shown the CH group is not written at the corners, and where some substituted atom or group is shown attached, the connection is to the C atom at that point.

FLUORAN.

Fluoran, $C_{20}H_{12}O_3$, may be considered the parent substance from which is derived a large number of colored and fluorescent compounds, such as fluorescein, eosin, etc. It contains three benzene rings (Fig. 5), and derivatives may be formed by the replacement of H atoms in any of these rings. Tetrachlorofluoran has four Cl atoms substituted for H atoms in the benzene ring 3 in the figure. Tetrabromotetrachlorofluoran has the further substitution of two Br atoms for hydrogen in each of the rings 1 and 2. The substitutions are seen to increase the absorption and shift the bands toward the visible without noticeably changing the frequency difference of the band centers.

FLUORESCEIN AND ITS DERIVATIVES.

Fluorescein may be thought of as derived from fluoran by the substitution of OH for H in each of the benzene rings 1 and 2. But because the substance is colored the structure usually assigned is that shown in the formula of Fig. 6, the "quinoid" structure being assumed for related colored compounds.

Tetrachlorofluorescein has four chlorine atoms in ring 3; eosin (tetra-

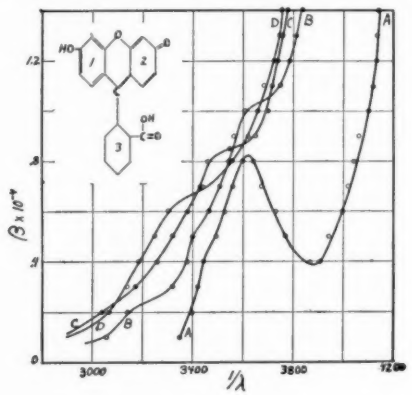


Fig. 6.

A, fluorescein; *B*, tetrachlorofluorescein, hydrate; *C*, eosin; *D*, tetrachloreosin.

bromofluorescein) has two Br atoms substituted in each of the rings 1 and 2; tetrachloreosin has both of the substitutions just mentioned. The curves show the shift toward the visible with increasing molecular weight.

The four neutral solutions were colored and all except fluorescein showed fluorescence. There is an evident difference in the form of the absorption curves for the fluorescent and non-fluorescent solutions, for which no reason can be given. Tetrachlorofluorescein was so slightly

soluble in neutral alcohol that tetrachlorofluorescein hydrate was used.

The addition to the fluorescein solution of four molecules of KOH for each molecule of fluorescein produced the well-known orange color and green fluorescence, accompanied by a marked increase in the absorption in both visible and ultra-violet (Fig. 7). With the addition of the alkali,

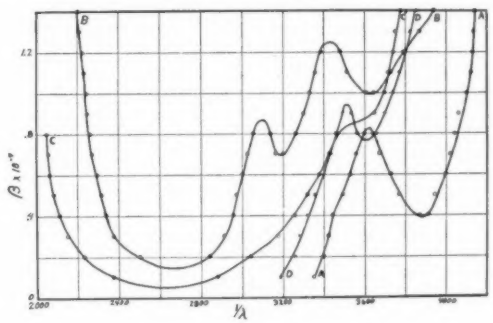


Fig. 7.

A, fluorescein, neutral solution; *B*, fluorescein, alkaline solution; *C*, eosin, neutral solution; *D*, eosin with trace of HCl.

two H atoms in the OH groups are replaced by K atoms, forming a colored salt of fluorescein. A similar replacement of hydrogen is effected upon the addition of KOH to most of the colorless solutions studied, visible absorption appearing and the ultra-violet absorption being modified. The author hopes to investigate the effect of gradually increasing the amount of alkali present, to determine whether the change in absorption is a progressive shift of absorption bands or is due to the disappearance of certain bands and the appearance of new ones.

A trace of HCl, added to the eosin solution, destroyed the yellow-green fluorescence and weakened the absorption (Fig. 7).

ORCINOLPHTHALEINS.

The orcinolphthaleins, a study of which has been published by Orndorff and Allen,[1] differ in constitution from fluorescein in the substitution of methyl groups for hydrogen (Fig. 8). The β-form is represented in the formula. Isomeric α- and γ-forms result from interchanges in the attachments of the OH and CH_3 groups. β-orcinoltetrachlorophthalein has four Cl atoms substituted in the lower benzene ring and tetrabromo-β-orcinolphthalein has two Br atoms in each of the upper rings. The neutral solutions are colorless, and their ultra-violet absorption spectra resemble that of fluorescein, though the center of the band is shifted

[1] Orndorff and Allen, Jour. Amer. Chem. Soc., 17, p. 1201, 1915.

toward the lower frequencies in the case of the heavier molecule. In this group also the heavier halogen causes the greater shift.

HYDROQUINONEPHTHALEIN.

This substance, though having the same percentage composition as fluorescein, differs structurally in having the two OH groups substituted at different places in the benzene rings. It is colorless. Its curve of

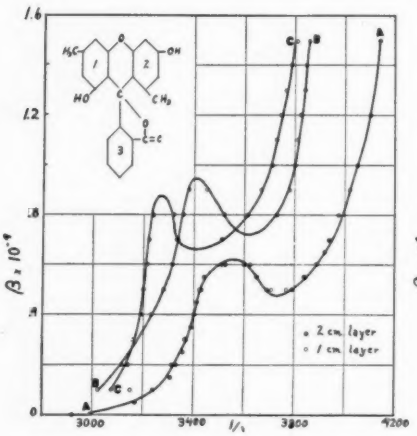


Fig. 8.

A, β-orcinolphthalein; *B*, β-orcinoltetrachlorophthalein; *C*, tetrabromo-β-orcinolphthalein.

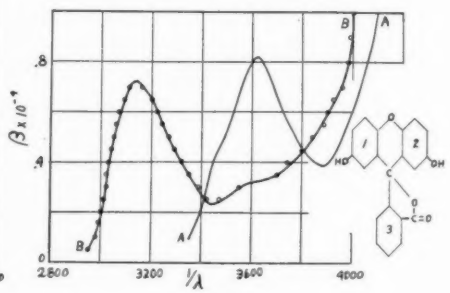


Fig. 9.

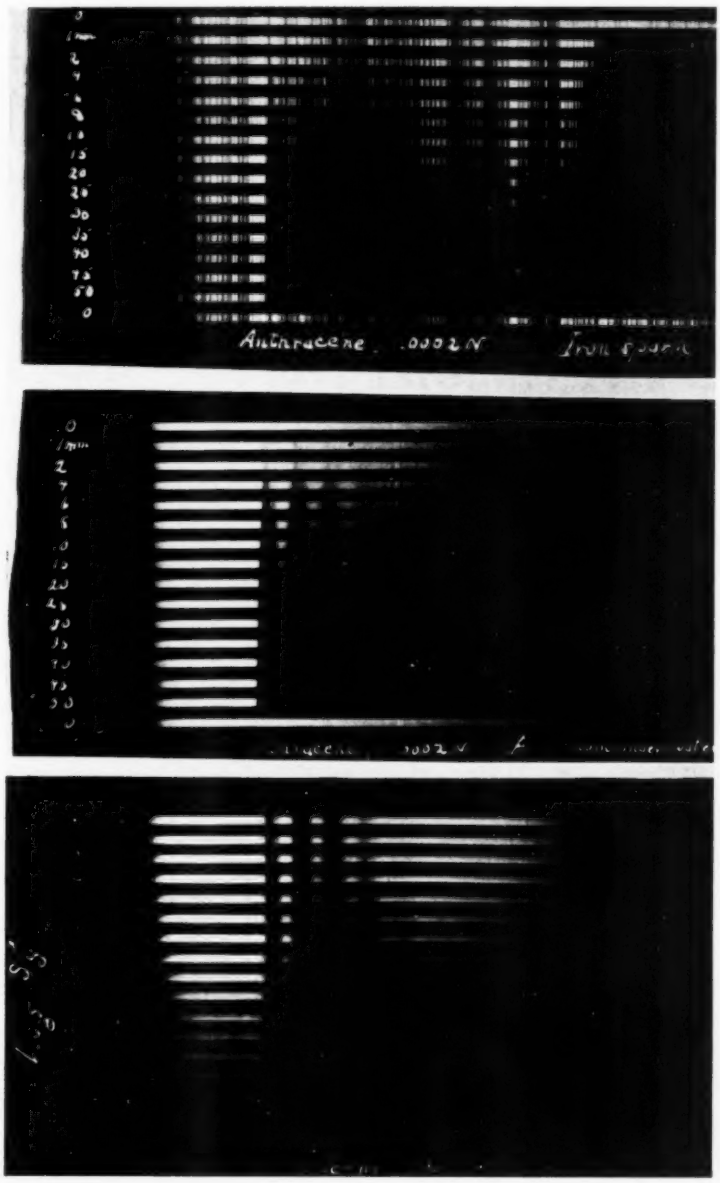
A, fluorescein; *B*, hydroquinonephthalein.

absorption (Fig. 9) resembles that of fluorescein in form, though the band appears at a lower frequency.

PHENOLPHTHALEINS.

Phenolphthalein lacks the bridge oxygen atom which joins the two similar benzene rings (Fig. 10). Being colorless, it is represented by a formula in which the ring 2 is not in the "quinoid" form shown in the fluorescein formula. Absorption curves for two groups of derivatives are shown. In the first group two halogen atoms are substituted in each of the upper rings. The negatives indicate a double band, with no change in the frequency difference of the band centers as the shift toward the visible takes place.

In each of the members of the second group of derivatives four Cl atoms are substituted in the lower benzene ring (Fig. 11), the substitutions in the upper rings being as in the first group. In the phenoltetrachlorophthaleins the absorption loses its definite banded appearance, the negatives showing only shoulders on the curves. This result, appear-



H. E. HOWE.

ing doubtful at first, was checked up by repetition with freshly purified samples.

All of these solutions become colored by the formation of potassium salts when KOH is added. The effect upon the ultra-violet spectrum will be reported in another paper.

As an example of a solution that does not become colored upon the

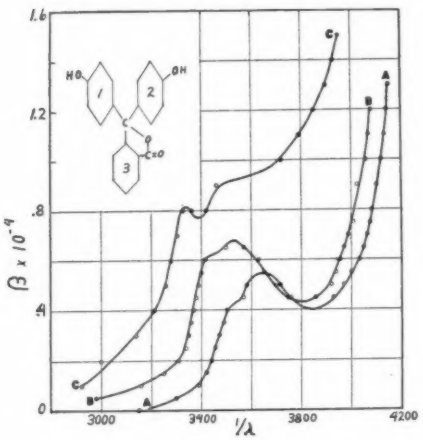


Fig. 10.

A, phenolphthalein; *B*, tetrabromophenolphthalein; *C*, tetraiodophenolphthalein.

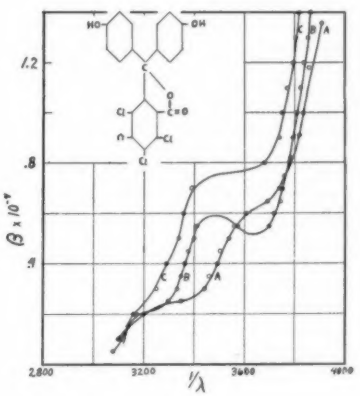


Fig. 11.

A, phenoltetrachlorophthalein; *B*, tetrabromophenoltetrachlorophthalein; *C*, tetraiodophenoltetrachlorophthalein.

addition of KOH, that of fluoran may be cited. The curve for a solution containing four molecules of KOH to each molecule of fluoran (Fig. 12)

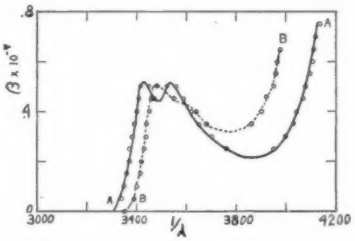


Fig. 12.

A, fluoran, four mol. KOH; *B*, fluoran in *N*/10 alcoholic KOH.

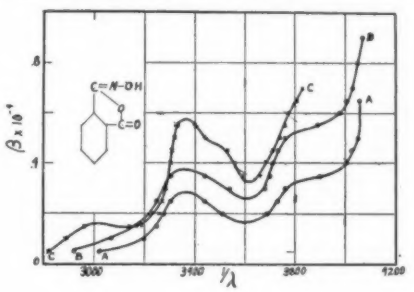


Fig. 13.

A, phthaloxime, white; *B*, phthaloxime, yellow; *C*, tetrachlorophthaloxime.

is not noticeably different from that of the neutral solution (Fig. 5). However, when fluoran was dissolved in a tenth normal alcoholic solution of KOH, a modified curve was obtained. This effect was not due to the solvent, as in this case the blank cell was filled with the alcoholic solution of KOH.

Fig. 13 gives curves taken for comparison with curves for the same substances, as obtained by Pratt[1] by the Baly-Detsch method. There is agreement as to the position of greatest absorption, but a difference as to which of the two isomeric forms absorbs most strongly.[2] The third curve in the figure shows the increase of absorption upon the addition of chlorine to the molecule.

The curves given in this paper show that the molecular absorption constant is of the same order of magnitude for solutions of compounds closely related structurally. All curves were made with solutions having concentrations between .0001N and .0002N. There is shown also the increasing absorption with increasing mass of the substituted groups.

In conclusion the writer wishes to thank Prof. W. R. Orndorff and Mr. S. A. Mahood for their advice concerning the study of the chemical compounds, all of which they have supplied. On the experimental side of the problem, the continued interest and frequent suggestions of Professors E. Merritt and R. C. Gibbs have been very helpful.

[1] Gibbs and Pratt, Phil. Jour. Sci., 8, p. 165, 1913.

[2] Because of the difference in the coördinates used in plotting, the author was unable to show the two sets of curves on one sheet.

THE DISTRIBUTION OF ANGULAR VELOCITIES AMONG DIATOMIC GAS MOLECULES.

BY EDWIN C. KEMBLE.

INTRODUCTION.

THE explanation of the structure of the infra-red absorption bands of gases given by Bjerrum[1] has led to a striking direct confirmation of the quantum theory in the form first proposed by Planck (assuming absorption as well as emission by quanta), and gives to the study of these bands a large significance for the further development of that theory. As this paper and the one which follows it are based on Bjerrum's ideas, a brief summary of the theory is given for the benefit of readers who may not have followed the original German papers containing its statement and the subsequent confirmation of its predictions.

As early as 1904 Drude,[2] from the study of the dispersion of various crystals, was led to the conclusion that the infra-red absorption and emission bands of most substances (including gases) must be due to the vibrations of electrically charged atoms and molecules rather than to the oscillations of the electrons inside the atoms. This view has been confirmed, in so far as it applies to solids, by the discovery that the frequencies of the reststrahlen can be roughly computed from the elastic constants of the crystals[3] and seems to be generally accepted by the workers in this field.

Nearly twenty-five years ago Lord Rayleigh[4] pointed out that if an oscillator which at rest emits and absorbs light of frequency ν_0, rotates with the frequency ν_r about an axis perpendicular to the direction of vibration, the emitted or absorbed light should be divided between the frequencies $\nu_0 + \nu_r$ and $\nu_0 - \nu_r$, and remarked that the absence of a corresponding broadening of the spectrum lines due to the molecular rotations constituted an outstanding difficulty in the theory of the

[1] Niels Bjerrum, Nernst Festschrift, Halle, 1912.

[2] P. Drude, Ann. d. Phys. (4), 14, p. 677, 1904.

[3] Cf., for example, E. Madelung, Nachrichten d. kgl. Ges. d. W. z. Göttingen (Math. Phys. Kl.), 20, p. 11, 1909; A. Einstein, "La Théorie du Rayonnement et les Quanta" (Proceedings of the First Solvay Conference), Paris, 1912, p. 413; W. Dehlinger, Phys. Zeit., 15, p. 276, 1914.

[4] Lord Rayleigh, Phil. Mag. (5), 34, p. 410, 1892.

breadth of these lines. Bjerrum (l. c.) has called attention to the fact that in the infra-red absorption spectra of gases a broadening of the magnitude to be expected from the molecular rotations does occur. He explains the sharpness of the lines in other parts of the spectrum by assuming, first, that unlike the infra-red bands the lines in the visible and ultra-violet are due to the vibrations of electrons inside the atoms, and second, that the atoms do not rotate with angular velocities comparable with those of the molecules.

Consider the infra-red absorption of a diatomic gas like HCl. If Drude's assumption is correct there should be but one absorption band (due to the vibration of the two atoms along their line of centers). It may be assumed that the rotation takes place only about axes perpendicular to the line of centers. If the distribution of angular velocities were in accordance with the classical statistical mechanics the band should be a doublet the maxima of which correspond to the most probable angular velocity of the molecules at the temperature in question. As a matter of fact the infra-red absorption spectrum of HCl does consist of just such a doublet, the maxima being at 3.40 μ and 3.55 μ at room temperature. From the separation of the maxima Bjerrum has made a rough computation of the moment of inertia of the molecule in the following manner.[1] Let λ' and λ'' be the wave-lengths of the two maxima. Then if ν_r is the corresponding frequency of molecular rotation

$$\nu_0 + \nu_r = c/\lambda' \tag{1}$$

and

$$\nu_0 - \nu_r = c/\lambda''. \tag{2}$$

Consequently,

$$2\nu_r = c\left(\frac{1}{\lambda'} - \frac{1}{\lambda''}\right). \tag{3}$$

Identify this frequency with that corresponding to the average energy of molecular rotation. Then, if J is the moment of inertia of the molecule,

$$2\pi^2\nu_r^2 J = RT/N,$$

or

$$J = \frac{RT}{2\pi^2\nu_r^2 N}, \tag{4}$$

where R is the gas constant and N is the number of molecules in a gram molecule. Bjerrum assumes the values

$$R = 0.83 \times 10^8, \quad N = 65 \times 10^{22}$$

and for $T = 291°$ computes

$$J = 5.4 \times 10^{-40} \text{ gm. cm.}^2$$

[1] N. Bjerrum, Verh. d. D. Phys. Ges., 16, p. 640, 1914.

Assuming that the masses of the atoms are concentrated in the nuclei we can compute the distance between the atomic centers from the moment of inertia.[1] The value so obtained is 1.84×10^{-8} cm., which is in satisfactory agreement with the molecular "diameters" computed from the kinetic theory of gases.[2]

Double bands of this character are very frequent in the infra-red spectra of gases.[3] In those cases tested the separation of the maxima varies with the temperature in accordance with Bjerrum's theory.[4]

Bjerrum predicted that the absorption bands of gases having more than two atoms per molecule would prove to be triplets, but his expectation has not been found to accord with the facts, as the absorption bands of water vapor and carbon dioxide, for instance, turn out to be doublets like those of the diatomic gases. Thus there is an outstanding difficulty with regard to the absorption of the more complex gases. However, this difficulty does not seem wholly insurmountable and the quantitative agreement of theory and experiment in the case of the diatomic gases leaves little doubt as to the fundamental soundness of Bjerrum's view.

The suggestion has been made by Lorentz[5] and Nernst[6] that according to the older form of Planck's theory a molecule ought not to be capable of rotating with any angular velocity whatever, but only with such angular velocities as make the energy an integral multiple of $h\nu$. According to this hypothesis the possible frequencies of rotation are those which satisfy the equation

$$\nu = \frac{nh}{2\pi^2 J}, \tag{5}$$

where n is any integer. Bjerrum has called attention to the fact that if this hypothesis is correct the absorption in the extreme infra-red (say beyond 50 μ) which we suppose is due to the *direct* action of the molecular rotations must be broken up into a series of equally spaced narrow bands, while the absorption bands in the near infra-red, due primarily to the atomic vibrations, must similarly be made up of a series of equally spaced fine lines which should appear when the bands are analyzed with an apparatus of sufficiently high resolving power. The predicted discon-

[1] Let m_1 and m_2 be the masses of the two atoms and let r_0 be the distance between the nuclei. Then $J = r_0^2 m_1 m_2/(m_1 + m_2)$.

[2] D. A. Goldhammer (Verh. d. D. Phys. Ges., 16, p. 715, 1914) estimates the "diameter" of the HCl molecule to be 3.0×10^{-8} cm.

[3] W. Burmeister, Verh. d. D. Phys. Ges., 15, p. 589, 1913.

[4] E. v. Bahr, Verh. d. D. Phys. Ges. 15, p. 710 and p. 731, 1913.

[5] H. A. Lorentz, "La Théorie du Rayonnement et les Quanta" (Proceedings of the First Solvay Conference), Paris, 1912, p. 447.

[6] W. Nernst, Zeit. f. Elektroch., 17, p. 265, 1911.

tinuities in both parts of the infra-red spectrum have been found.[1] The moment of inertia of the HCl molecule has been computed by means of (5) and the value obtained in this way has been found to agree with that computed from the separation of the maxima of the double band. *Great as are the difficulties to which we are led by that form of the quantum theory which assumes that both absorption and emission take place by quanta, it would appear that there is little hope of escape from this essentially kinematical confirmation of that theory.*

For further details regarding Bjerrum's theory and its experimental confirmation the reader is referred to the original papers.

In addition to (5) the following formula for the possible frequencies of rotation of a molecule on the basis of the quantum theory has been proposed by Ehrenfest.[2]

$$\nu = \frac{nh}{4\pi^2 J}. \tag{6}$$

(6) differs from (5) by a factor of two which comes from the fact that Ehrenfest assumes that the quantum for rotations is not $h\nu$ but $\frac{1}{2}h\nu$. He says that this substitution of $\frac{1}{2}h\nu$ for $h\nu$ can be justified from a very general point of view, but gives no further explanation. (Planck's generalization of the quantum theory to cover systems having several degrees of freedom[3] also leads to (6)).

However that may be, Bjerrum has taken the very close agreement between the values of J computed from (5) and from the separation of the maxima of the absorption bands doubled by the molecular rotations as evidence that (5) and not (6) is the correct formula.[4] In this paper we propose to show that the approximation made by Bjerrum in computing the moment of inertia from the separation of the maxima of the double band in the infra-red spectrum of HCl was not so good as he supposed and that if the computation is correctly made it turns out that the resulting value of J checks with that obtained from (6) and not with that obtained from (5).

We will also show that the shape of the carbon monoxide absorption band at 4.6 μ is such as to give direct proof that the law of the distribution of angular velocities among the molecules at room temperature is that predicted by the classical statistical mechanics (except, of course, that the distribution is not continuous).

[1] Cf. N. Bjerrum, Nernst Festschrift, Halle, 1912 and Verh. d. D. Phys. Ges., 16, p. 640, 1914; A. Eucken, Verh. d. D. Phys. Ges., 15, p. 1159, 1913; E. v. Bahr, l. c.

[2] P. Ehrenfest, Verh. d. D. Phys. Ges., 15, p. 451, 1913; A. Eucken, l. c.

[3] M. Planck, Verh. d. D. Phys. Ges., 17, pp. 407 and 438, 1915.

[4] N. Bjerrum, Verh. d. D. Phys. Ges., 16, p. 640, 1914.

DEDUCTION OF THE VALUE OF THE MOMENT OF INERTIA FROM THE SEPARATION OF THE ABSORPTION MAXIMA.

The roughness of Bjerrum's approximation consisted in identifying the angular velocity corresponding to the maxima of the absorption doublet, *i. e.*, the most probable angular velocity, with the angular velocity corresponding to the average energy. This makes a considerable difference in the case of the linear velocities of the molecules or of the angular velocities among molecules capable of rotating about three mutually perpendicular axes, but it makes a much greater difference if, as in the case of HCl, the molecule has only two rotational degrees of freedom.

In what immediately follows it will be assumed that at ordinary room temperatures the distribution of angular velocities among the molecules is in accordance with the classical statistical mechanics, the justification for this hypothesis being given later. The molecule is treated as a pair of heavy particles rigidly joined together.

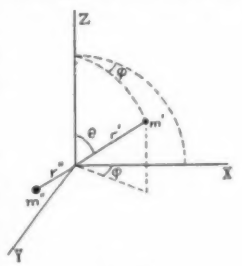


Fig. 1.

Let the masses of the atoms in a diatomic molecule be m' and m''. The positions of the nuclei with reference to a set of axes fixed in direction and having its origin at the center of mass of the molecule will be specified by the spherical coördinates r', r'', θ, φ (Fig. 1). Then the rotational energy is easily shown to be

$$\epsilon_r = \tfrac{1}{2}(m'r'^2 + m''r''^2)(\dot{\theta}^2 + \sin^2\theta\cdot\dot{\varphi}^2) = (J/2)(\dot{\theta}^2 + \dot{\varphi}^2\sin^2\theta). \quad (7)$$

$\dot{\theta}$ and $\dot{\varphi}\sin\theta$ are the components of the angular velocity in and perpendicular to the xy plane respectively. It is therefore convenient to denote them by ω' and ω'', so that

$$\epsilon_r = \tfrac{1}{2}J(\omega'^2 + \omega''^2) \equiv \tfrac{1}{2}J\omega^2. \quad (8)$$

Consider a Gibbs canonical ensemble of systems, each of which is made up of μ diatomic molecules. In the notation of Gibbs, in which the coördinates are denoted by q's and the momenta by p's, the chance that a system chosen at random will fall into any particular element of extension in phase,

$$dp_1, \cdots dp_n, \quad dq_1, \cdots dq_n,$$

is

$$dP = e^{(\psi-\epsilon)/\Theta}dp_1, \cdots dp_n, \quad dq_1, \cdots dq_n.^1 \quad (9)$$

Here ψ and Θ are constants, the latter being the modulus of the ensemble

[1] Cf. J. W. Gibbs, Elementary Principles in Statistical Mechanics, p. 33.

(*i. e.*, RT/N). ϵ is the energy corresponding to this element of extension in phase.

The phase of each molecule will be specified by five coördinates, viz., θ, φ, and the coördinates of the center of mass, together with the corresponding momenta. The coördinates and momenta which specify the positions and velocities of the centers of mass may be eliminated by integrating over all possible values of these quantities. Denote the various molecules in any one system by the subscripts 1, 2, $\cdots \mu$. Then the chance that a system chosen at random will lie within the region

$$d(p_\theta)_1,\ d(p_\phi)_1,\ d(p_\theta)_2 \cdots d(p_\phi)_\mu,\ d\theta_1 \cdots d\varphi_\mu$$

is

$$dP = Ce^{(\psi-\epsilon)/\Theta} d(p_\theta)_1 \cdots d\varphi_\mu, \tag{10}$$

where

$$(p_\theta)_i = \frac{\partial \epsilon}{\partial \dot{\theta}_i} = J\dot{\theta}_i = J\omega_i'$$

and

$$(p_\phi)_i = \frac{\partial \epsilon}{\partial \dot{\varphi}_i} = J \sin^2 \theta_i \cdot \dot{\varphi}_i = J\omega_i'' \sin \theta.$$

In order to obtain the law of the distribution of velocities from (10) it is necessary to change the independent variables from $(p_\theta)_i$, $(p_\phi)_i$, θ_i, φ_i, to ω_i', ω_i'', θ_i, φ_i. We have

$$\begin{aligned} d(p_\theta)_i d(p_\phi)_i d\theta_i d\varphi_i &= \left| \frac{D[(p_\theta)_i (p_\phi)_i, \theta_i, \varphi_i]}{D[\omega_i'', \omega_i', \theta_i, \varphi_i]} \right| d\omega_i'' d\omega_i' d\theta_i d\varphi_i \\ &= J^2 \sin \theta_i d\omega_i'' d\omega_i' d\theta_i d\varphi_i. \end{aligned} \tag{11}$$

Then (10) becomes

$$dP = Ce^{\psi/\Theta} J^{2\mu} \sin \theta_1 \cdots \sin \theta_\mu e^{-(\epsilon/\Theta)} d\omega_1'' \cdots d\omega_1' \cdots d\omega_\mu' d\theta_1 \cdots d\varphi_\mu. \tag{12}$$

Let ϵ' denote that part of the energy not due to the rotations. Then

$$\epsilon = \sum_{i=1}^{\mu} \tfrac{1}{2} J(\omega_i'^2 + \omega_i''^2) + \epsilon' = \sum_{i=1}^{\mu} \tfrac{1}{2} J\omega_i^2 + \epsilon'.$$

The chance that in a system chosen at random the νth molecule will have an angular velocity in the elementary region $d\omega' d\omega''$ is

$$\begin{aligned} Ce^{-J/2\Theta(\omega'^2+\omega''^2)} d\omega_\nu' d\omega_\nu'' \Big[\int_{\text{values}}^{\text{all}} \cdots \int e^{1/\Theta\{\psi - \Sigma' \frac{1}{2} J\omega^2 - \epsilon'\}} \\ \times J^{2\mu} \sin \theta_1 \cdots \sin \theta_\mu d\omega_1'' \cdots d\varphi_\mu \Big], \end{aligned} \tag{13}$$

where Σ' denotes summation over all the molecules but one. The integral is independent of ν and of the region element under consideration. Hence it may be treated as a constant. Denote the product of C into this integral by C'. Then the most probable value of the total number

of molecules having their velocities in the elementary region $d\omega' d\omega''$ is

$$\mu C' e^{-(J/2\Theta)(\omega'^2+\omega''^2)} d\omega' d\omega''. \tag{14}$$

The numerical value of C' may be determined from the equation

$$\mu = \mu C' \int\int e^{-(J/2\Theta)(\omega'^2+\omega''^2)} d\omega' d\omega''.$$

It is

$$C' = \frac{J}{2\pi\Theta}.$$

If ω' and ω'' be regarded as rectangular coördinates the corresponding polar coördinates are

$$\omega \equiv \sqrt{\omega'^2 + \omega''^2},$$

and

$$\chi = \tan^{-1}\left(\frac{\omega'}{\omega''}\right).$$

Then the region element $d\omega' d\omega''$ may be replaced by $\omega d\omega d\chi$. The most probable value of the number of molecules whose resultant angular velocity lies between ω and $\omega + d\omega$ is

$$\frac{\mu J}{\Theta} e^{-\frac{J\omega^2}{2\Theta}} \cdot \omega d\omega. \tag{15}$$

(15) is an expression of the distribution law for angular velocities in a diatomic gas. The corresponding expression for the law of the distribution of linear velocities is

$$\sqrt{\frac{2m^3}{\pi\Theta^3}} e^{-\frac{mv^2}{2\Theta}} \cdot v^2 dv.$$

We desire to compute from (15) the ratio of the most probable angular velocity to the angular velocity corresponding to the average energy. The most probable angular velocity is that for which

$$\frac{d}{d\omega}(\omega e^{-\frac{J\omega^2}{2\Theta}}) = e^{-\frac{J\omega^2}{2\Theta}} - \frac{J\omega^2}{\Theta} e^{-\frac{J\omega^2}{2\Theta}} = 0.$$

Let Ω be a root of this equation. Then

$$\Omega = \pm\sqrt{\frac{\Theta}{J}}. \tag{16}$$

The average energy of rotation is

$$\bar{\epsilon}_\omega = \frac{J}{\Theta}\int_0^\infty e^{-\frac{J\omega^2}{2\Theta}} \cdot \frac{J\omega^2}{2} \cdot \omega d\omega = \Theta. \tag{17}$$

Hence

$$\Omega = \pm\sqrt{\frac{\bar{\epsilon}_\omega}{J}} = \pm\sqrt{\frac{RT}{JN}}.$$

Let ν_r denote the corresponding frequency. Then we have

$$J = \frac{RT}{4\pi^2 \nu_r^2 N} \tag{18}$$

instead of (4). Accordingly the moment of inertia of the HCl molecule is

$$J = 2.7 \times 10^{-40} \text{ gm. cm.}^2$$

This checks with (6) exactly as the value computed by Bjerrum checked with (5).[1]

Rotation Frequencies of the HCl Molecule.

Observed E. v. Bahr.	n.	Computed by (6).
0.745×10^{12}	1	0.6×10^{12}
1.395	2	1.2
2.015	3	1.8
2.62	4	2.4
3.20	5	3.0
3.68	6	3.6
4.08	7	4.2

EXPERIMENTAL PROOF OF THE VELOCITY DISTRIBUTION LAW.

As a check on our theory of the structure of the infra-red absorption bands it is of interest to compare the form of the absorption curve predicted by (15) with that found experimentally by Burmeister (l. c.), who has investigated the infra-red absorption spectra of a number of the simpler gases with great care.

We have already called attention to the fact that a molecule whose frequency of oscillation is ν_0 and whose frequency of rotation is ν_r will emit or absorb light of the frequencies $\nu_0 + \nu_r$ and $\nu_0 - \nu_r$. Let us call these the effective frequencies of the molecular vibration. We assume that the ability of a molecule to absorb light is not affected by its rotary motion. Then the absorption coefficient of the gas in the frequency interval between ν_0 and $\nu + \Delta\nu$ should be proportional to the number of molecules which have effective frequencies in that interval. Consequently if (15) gives the distribution law correctly the curve obtained when the absorption coefficient is plotted against frequency should be of the form

$$\alpha = \pm a e^{-b(\nu - \nu_0)^2}(\nu - \nu_0). \tag{19}$$

Of course the discontinuities which have been found in the absorption bands show that (19) cannot be strictly accurate. What we may really expect is a series of equally spaced narrow absorption bands having such

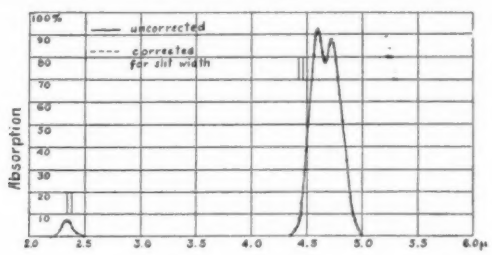
[1] The following table (taken from Bjerrum, l. c.) gives the observed rotation frequencies together with the values computed by means of (6) and (18). The small systematic error is presumably due to the variation of J with the frequency of rotation.

relative intensities that a curve of the form (19) is their envelope. The number of molecules whose effective frequencies lie in the interval between ν and $\nu + \Delta\nu$ will be proportional to

$$(\nu - \nu_0)e^{-b(\nu-\nu_0)^2}$$

only if that interval is large enough to cover a number of these elementary bands or lines. However, the absorption curve obtained with an apparatus whose resolving power is insufficient to separate these elementary bands should be of the form (19).

The curves given by Burmeister (cf. Fig. 2) show the total observed absorption in tubes of 20 cm. or of 40 cm. length plotted as a function of the wave-length. The two pairs of short vertical lines indicate the wave-length interval subtended by the slit. We have first to compute the values of the absorption coefficient corresponding to the various observed total absorptions. This would be easy enough if the various bundles



Infra-red Absorption of Carbon Monoxide (after Burmeister).

Fig. 2.

of rays examined were sufficiently homogeneous so that the absorption coefficient for all frequencies in any one bundle could be regarded as constant. Let I_0 denote the initial intensity of such a bundle and let I denote its intensity after passing through L centimeters of absorbing gas. Then under the ideal conditions specified

$$I = I_0 e^{-aL} \tag{20}$$

and the absorption coefficients are proportional to the values of $\log I/I_0$. But in Burmeister's experiments the resolving power of the spectrometer was not sufficient to separate the band into the lines which compose it. Consequently the light passing through the slit at any one time was not of sufficient homogeneity so that all parts of it were absorbed with equal readiness. Under these conditions the total energy of the beam does not vary according to (20). In fact the discontinuous character of the infra-red absorption bands was first proved by observing the failure of the absorption law (20).[1]

[1] E. v. Bahr, Verh. d. D. Phys. Ges., 15, p. 710, 1913.

We have data showing the actual absorption law for the complex beams under consideration only in the case of one of the diatomic gases whose absorption bands were studied by Burmeister, viz., CO. In Fig. 3 we reproduce an experimental curve due to Dr. v. Bahr (l. c.) showing the relation between the total absorption in per cent. and the partial pressure of the absorbing carbon monoxide. This is of the same form as the curve connecting the absorption in per cent. with the length of tube for constant partial pressure. The dotted portion of the curve is

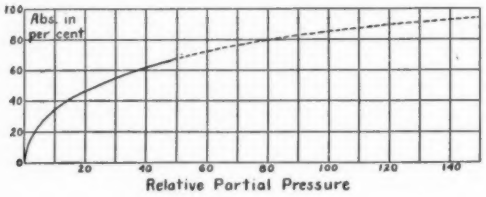


Fig. 3.

an extrapolation which should be fairly accurate as it was obtained with the help of an asymptote (the 100 per cent. absorption line). The initial slope of the curve is a measure of the average absorption coefficient of the different wave-lengths in the beam. Dr. v. Bahr reports that this curve is of the same form whether the slit used is comparatively narrow or wide enough to take in the whole band. We conclude that it would be the same for a narrow slit set to cover any portion of the band. By the statement that two or more absorption curves are of the same form we mean that the curves can be made to coincide by a suitable change of the scales which indicate the lengths of the absorption paths. Then to get the absorption curve for one frequency interval from that for another, we must multiply the abscissæ of the given curve by a number so chosen that the ratios of the absorptions from the two intervals in the same length of tube shall check with the corresponding ordinates of Burmeister's curve. The initial slopes or absorption coefficients for different curves will be inversely proportional to these multipliers. It follows that the absorption coefficients corresponding to two different values of the total absorption are directly proportional to the abscissæ corresponding to these absorptions on Dr. v. Bahr's curve.

In this manner the writer has obtained a curve of absorption coefficients from the curve of total absorptions of the double band at 4.6 μ given by Burmeister. The reader will observe (Fig. 2) that the latter curve is unsymmetrical, the absorption being greater on the high frequency side. This lack of symmetry is much greater in the curve of absorption coefficients and is at present wholly unexplained.[1] The absorption coefficients

[1] We should expect a difference proportional to the difference in the squares of the effective frequencies but this is small.

of symmetrically situated points have therefore been averaged. The resulting average absorption coefficient plotted against the corresponding angular velocity (in arbitrary units) is shown in Fig. 4, Curve *a*. Curve *b* is plotted from the equation

$$y = 299.5\, xe^{-x^2}$$

(cf. equation 19). Curve *c* shows the distribution law predicted by

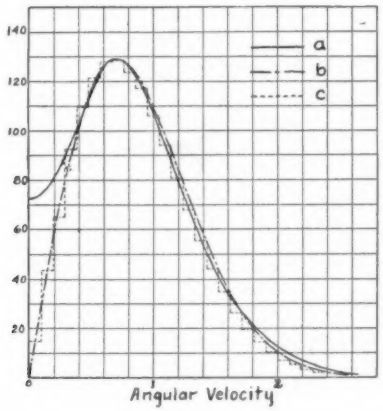


Fig. 4.

Planck (l. c., p. 4) on the basis of his later form of the quantum theory. (Curve *c* could be made to fit the experimental curve somewhat better by a slightly different choice of moment of inertia.) The agreement between the experimental and theoretical curves seems to the writer remarkably good under the circumstances. The discrepancy at zero angular velocity is undoubtedly due largely to the wide slit used. The values of the total absorption have been corrected for slit width according to Runge's formula but this formula would not apply at this point where the change in the absorption coefficient is discontinuous.

The agreement between the experimental and theoretical curves justifies the assumption of the distribution law (15) in computing the moment of inertia of the HCl molecule. Apparently the true distribution law is to be obtained by some small modification of Planck's extension of the quantum theory to systems having several degrees of freedom so as to adapt that extension to the hypothesis of discontinuous absorption.

SUMMARY.

We have developed a formula for the distribution of angular velocities among diatomic gas molecules on the basis of the classical statistical mechanics and have shown that this formula is in agreement with the

observed shape of the band at 4.6 μ in the infra-red absorption spectrum of carbon monoxide (the only diatomic gas for which the necessary data are available).

On the basis of this distribution law we have shown that the expression for the moment of inertia of a diatomic molecule in terms of the frequency of rotation ν_r corresponding to the maxima of a Bjerrum double band is

$$J = \frac{RT}{4\pi^2 \nu_r^2 N}$$

and not

$$J = \frac{RT}{2\pi^2 \nu_r^2 N}.$$

We have shown that this new formula for the moment of inertia checks with Ehrenfest's assumption that the quantum for the rotational energy should be $\frac{1}{2}h\nu$ instead of $h\nu$.

JEFFERSON PHYSICAL LABORATORY,
HARVARD UNIVERSITY,
August 7, 1916.

ON THE OCCURRENCE OF HARMONICS IN THE INFRA-RED ABSORPTION SPECTRA OF GASES.

BY EDWIN C. KEMBLE.

INTRODUCTION.

IN the preceding paper on "The Distribution of Angular Velocities among Diatomic Gas Molecules" we have given a brief account of Bjerrum's theory of the structure of the infra-red absorption bands of gases and of the direct and conclusive evidence which that theory has given in favor of that older form of the quantum theory according to which the vibrating atoms and electrons can have only energies which are integral multiples of $h\nu$ (the rotational energies, on the other hand, being multiples of $h\nu/2$). The application of this theory to the vibrations of the atoms in a diatomic gas molecule shows that the minimum amplitude of these oscillations must be an appreciable fraction of the mean distance between the atomic centers. In the present paper we propose to show that owing to the large amplitude of these oscillations and the nonlinearity of the law of force between the atoms it is to be expected that the strong infra-red absorption bands to which these vibrations give rise should be accompanied by faint harmonics. Such an harmonic does occur in the infra-red spectrum of carbon monoxide and we will give a number of reasons for believing that its occurrence is not accidental. Another result of the application of this form of the quantum theory to these atomic vibrations is the prediction of new infra-red absorption bands at high temperatures. In conclusion we will give some new evidence from the width of these bands in favor of the hypothesis that the vibratory energy must be a multiple of $h\nu$.

REASON FOR THE OCCURRENCE OF FAINT HARMONICS.

Consider the vibratory motion of the atoms in a diatomic gas molecule. The restoring force will not be strictly proportional to the relative displacement from the position of equilibrium. Consequently, while the motion will be periodic no matter what the amplitude,[1] it will be approximately simple harmonic only for very small amplitudes. The accelera-

[1] This would not be true if the motion were damped by radiation, but of course there can be no such damping if the process of radiation is discontinuous.

tion corresponding to such a periodic non-sinusoidal motion of frequency ν, if it be expressed by means of circular functions at all must be expressed as a Fourier's series in sines and cosines of integral multiples of $2\pi\nu t$.

Turn for a moment to the radiation and absorption in the extreme infra-red due to the rotation of the polarized molecules. According to the classical mechanics and electrodynamics we should expect that as a rotating molecule absorbs energy its frequency of rotation should increase and with that the frequency of the radiation absorbed. Whether the radiation be absorbed by quanta or not we should expect that the molecule would absorb light of all frequencies between that of its rotation before absorption and that of its rotation after absorption. But as a matter of fact the absorption seems to be all from a small frequency interval in the immediate neighborhood of the final frequency of rotation. This fact seems to make plausible the general assumption that *the character of the radiation emitted or absorbed by an oscillator is determined by the character of the motion of the atoms before emission begins or after absorption has taken place.*

It follows at once from this assumption that *the radiation or absorption from a non-sinusoidal periodic oscillation should consist of an infinite series of lines of gradually decreasing intensity whose frequencies are integral multiples of the frequency of the fundamental* (each term in the above-mentioned Fourier's series giving rise to a line). Of course we should hardly expect that more than two or three of the harmonics would have sufficient intensity to be detected experimentally.

Another consequence of the lack of linearity in the relation between the restoring force and the displacement is that the frequency of vibration depends on the amplitude. This point will be taken up again later on.

It is not difficult to show that the departure of the motion from the simple harmonic type must be considerable. Consider the vibratory motion of the atoms in a diatomic molecule having one quantum of energy. It will be assumed that the motion takes place in accordance with the classical mechanics. Let m_1 and m_2 be the masses of the two atoms and let r denote the distance between the nuclei. Let $F(r)$ denote the force exerted by each atom on the other, a repulsion being taken as positive. Then it may very easily be shown that the equation of motion is

$$m\frac{d^2r}{dt^2} = F(r), \tag{1}$$

where

$$m = \frac{m_1 m_2}{m_1 + m_2}. \tag{1a}$$

Let r_0 denote the value of r for which the force vanishes, *i. e.*, the distance between the nuclei when the two atoms are in equilibrium and write

$$x = r - r_0.$$

Expanding $F(r)$ in a Taylor's series we may throw (1) into the form

$$m\frac{d^2x}{dt^2} = x\left(\frac{dF}{dr}\right)_{r=r_0} + \frac{x^2}{2!}\left(\frac{d^2F}{dr^2}\right)_{r=r_0} + \frac{x^3}{3!}\left(\frac{d^3F}{dr^3}\right)_{r=r_0} + \cdots. \quad (2)$$

For sufficiently small values of x the terms after the first will always be negligible and the force will be a linear function of the displacement. But if the displacements are not small the terms of higher order than the first must be taken into account. However, we may obtain an approximate idea of the amplitude of the oscillation if we neglect these higher order terms. Let A denote this unknown amplitude. Then the approximate value of the energy will be $2\pi^2 m\nu^2 A^2$. Equating the energy to $h\nu$ we obtain

$$A = \frac{1}{\pi}\sqrt{\frac{h}{2m\nu}}. \quad (3)$$

HCl is a typical diatomic gas. It has a single infra-red absorption band, a doublet with maxima at 3.40 μ and 3.55 μ respectively. The corresponding fundamental frequency is 8.64×10^{13} vibrations per second. Substituting the masses of the hydrogen and chlorine atoms for m_1 and m_2 respectively we obtain

$$m = \frac{35.5 \times 1.64 \times 10^{-24}}{35.5 + 1.0} = 1.60 \times 10^{-24} \text{ gm.}$$

If 6.4×10^{-27} be taken as the value of h, the amplitude computed from (3) is 1.53×10^{-9} cm., or about 12 per cent. of the normal distance between the nuclei.[1]

We are of course ignorant of the exact form of the law of force, but it is obvious that it cannot be even approximately linear for such large relative displacements as that just computed. The common assumption regarding the law of intermolecular repulsion is that it is of the form

$$f(r) = Ar^{-n}, \quad (4)$$

where n is a positive number. The values suggested for n vary from five

[1] The moment of inertia of the HCl molecule is 2.7×10^{-40} gm. cm.^{2} (cf. preceding paper on "The Distribution of Angular Velocities Among Diatomic Gas Molecules"). Assuming that the masses m_1 and m_2 of the two atoms are concentrated in the nuclei whose distance apart is r_0 we obtain the expression

$$J = \frac{m_1 m_2}{m_1 + m_2} r_0^2$$

for the moment of inertia. Substituting into this formula the numerical values of J, m_1 and m_2 and solving for r_0 we obtain $r_0 = 1.30 \times 10^{-8}$ cm.

to fifteen. It seems plausible to assume for the law of interatomic force the analogous form

$$F(r) = ar^{-n} - b.^1 \tag{5}$$

Giving n the small value 5 and expanding in series we obtain

$$F(r_0 + \Delta r) = -5ar_0^{-6}\Delta r + 30ar_0^{-7}\frac{(\Delta r)^2}{2!} - 210ar_0^{-8}\frac{(\Delta r)^3}{3!} + \cdots.$$

Put

$$\Delta r = -0.12r_0.$$

Then the ratio of the second degree term to the first degree term takes the value 0.36 and the ratio of the third degree term to the first degree term becomes 0.11. The ratio of the sum of the first three nonlinear terms to the linear terms is 0.48. In other words, if the law of force were as assumed, the force acting between the atoms at this extremity of the vibration would be half again as great as that computed on the assumption that the force is a linear function of the displacement. For larger values of n the effect of the nonlinear terms would be even greater.

This preliminary computation is for a molecule having a single quantum of vibratory energy. But the ratio of the number of molecules which have one quantum of vibratory energy at the temperature T to the number which have no vibratory energy is $e^{h\nu/kT}$. The numerical value of this ratio for HCl at 18° C. is 1.5×10^6. This is also the ratio of the number which have one quantum to the number which have two. Consequently practically all the absorption must be due to the molecules which are taking up their first quantum of vibratory energy and the character of the radiation absorbed must be determined by the character of the vibration corresponding to one quantum of energy.

EXPERIMENTAL CONFIRMATION.

Perhaps the most careful investigation of the infra-red absorption spectra of the simpler gases made thus far was that of Burmeister.[2] He examined four diatomic gases, Cl_2, HCl, Br_2 and HBr, between the wavelengths 1 μ and 18 μ with great care. Investigation of the absorption in certain regions of the infra-red spectra of three other diatomic gases, H_2, O_2 and CO, was also made and these observations together with those of other investigators give exact information regarding the infra-red absorption spectra of these gases over the region in which the first four were examined. Considerable pains were taken to eliminate impurities.

[1] The attractive force b is probably not constant but its rate of variation must be small compared with that of the repulsive force.

[2] W. Burmeister, Verh. d. D. Phys. Ges., 15, p. 589, 1913.

None of the gaseous elements, H_2, O_2, Cl_2, Br_2, has any infra-red absorption bands. In view of Drude's theory of the origin of these bands[1] this is not surprising, for it is not to be expected that the atoms in these otherwise symmetrical molecules should turn out to bear charges of opposite sign. In fact the absence of infra-red absorption bands in the spectra of these elementary gases is a confirmation of the view that the bands in this region are due wholly to atomic vibrations, for it shows that these bands are peculiar to those gases whose atoms are charged. HCl and HBr have each but one double absorption band. CO has a strong double band with maxima at 4.60 μ and 4.72 μ and a weak band with a single observed maximum at 2.35 μ.[2]

The writer is of the opinion that the occurrence of a weak band in the absorption spectrum of carbon monoxide at nearly half the mean wave-length of the strong dobule band near 4.60 μ is not accidental, but is a true example of the kind of harmonics predicted by our theory.

As evidence in favor of this view we observe in the first place that the band meets the three *necessary* conditions imposed by the theory. (*a*) The wave-length is right. A careful remeasurement of Burmeister's absorption curve indicates that the maximum of the faint band is nearer 2.34 μ than 2.35 μ. The wave-length corresponding to the mid-point between the maxima of the double band is 4.66 μ. Thus the discrepancy between the half wave-length of the strong band and the wave-length of the weak band is only 0.01 μ, an amount easily within the limit of experimental error. (*b*) The relative intensity of the two bands is right, *i. e.*, the fundamental is much more intense than the harmonic. (*c*) The character of the harmonic agrees with that of the fundamental. Both bands are fairly symmetrical and their relative widths check fairly well with the theory. The formula for the separation of the two components into which any line is split by the molecular rotation[3] shows that this separation should be proportional to the square of the average wave-length. Consequently the width of the harmonic should be one fourth of the width of the fundamental. Measurement of Burmeister's curves shows that the band at 2.34 μ is actually about one third the width of that at 4.66 μ. The correction to be made to pass from total absorption to absorption coefficient increases the discrepancy, but on account

[1] Cf. introduction to the preceding paper on "The Distribution of Angular Velocities, etc."

[2] Cf. Fig. 2 of the preceding paper.

[3] The formula is

$$\lambda_1 - \lambda_2 = 2\frac{\lambda_1\lambda_2}{\lambda_r},$$

where λ_1 and λ_2 are the wave-lengths of the two components and λ_r is the wave-length corresponding to the most probable frequency of rotation. (Cf. preceding paper on "The Distribution of Angular Velocities among Diatomic Gas Molecules.")

of the low dispersion, which was quite insufficient to separate the components of the harmonic, the determination of its width is so uncertain that the agreement between theory and experiment on this point need not be considered unsatisfactory.

A second reason for believing that the band at 2.34 μ is a true harmonic of the one at 4.66 μ is the difficulty in accounting for the former in any other way. A diatomic molecule can have but one atomic vibration. Therefore, if the band at 2.34 μ is not a bonafide harmonic of the band at 4.66 μ, it must be due either to an impurity or to an electronic vibration inside the atom. The care with which Burmeister tested these bands seems to rule out the first alternative. There are two reasons for supposing that this band is not due to an electronic vibration. In the first place, absorption bands not due to atomic vibrations in the infra-red spectra of diatomic gases between, say, 1.5 μ and 15 μ are rare, if they occur at all. In none of the seven diatomic gases examined by Burmeister with the exception of CO is there more than the one band due to the atomic vibration. More generally, it is possible to predict from the number of atoms in the more complicated molecules the number of normal modes of vibration which the atoms should have and in none of the absorption spectra of the four gases examined by Burmeister having three or more atoms per molecule are there more bands than there are modes for the corresponding molecules. Coblentz[1] found exceptions to this rule in the gases H_2S, SO_2 and NH_3 but the extra lines which he noted may be due to impurities against which he could not guard so completely in his very extensive survey of absorption spectra or (as some of the lines are faint) they may be due to the nonlinearity of the law of force.[2] The other reason for supposing that the band at 2.34 μ in the spectrum of CO is not due to an electronic vibration is that like the other infra-red absorption bands under discussion it has a different character from that usual among the bands in the visible.[3] The latter generally have a strong head from which they gradually fade away on one side or have a wavy fluctuation in intensity.

[1] W. W. Coblentz, Investigations of Infra-red Spectra, Washington, 1905.

[2] It does not follow from the fact that the failure of Hook's law for large vibrations in a diatomic molecule introduces new absorption and emission bands which are harmonics of the fundamental that the same rule holds for molecules having three or more atoms. In the case of the diatomic molecules the motion is necessarily strictly periodic for any amplitude and for this reason the acceleration may be analyzed into a Fourier's series of sine functions of integral multiples of $2\pi\nu t$. But apparently the motion of more complicated atomic systems need not follow this rule and it may be that the effect of the failure of Hook's law is in this case to introduce faint absorption bands which are not harmonics of the fundamental bands corresponding to the normal modes of oscillation for infinitesimal energies.

[3] See, for instance, Konen, Das Leuchten der Gase und Dämpfe, Braunschweig, 1913, p. 245.

The writer has also examined the charts given by Coblentz in his "Investigations of Infra-red Spectra" for other cases of harmonic absorption bands. Coblentz himself, after remarking that a search for harmonic absorption bands is generally considered illusory, calls attention to their frequent occurrence in the infra-red spectra of the organic substances examined by him. For instance, a great many hydrocarbons show a very strong band at 3.4 μ and a weak one at about 1.7 μ. Thiophene shows a strong band at 9.29 μ and a weak one at 4.60 μ. Acetylene shows similar bands at 7.4 μ and 3.7 μ; butane at 8.90 μ and 4.45 μ; ethylene at 10.5 μ and 5.27 μ; carvacrol at 12.3 μ and 6.13 μ with another pair of bands at 10.09 μ and 5.04 μ and still another at 8.08 μ and 4.01 μ; ethyl iodide at 10.5 μ and 5.28 μ; methyl acetate at 9.6 μ and 4.78 μ; selenite at 2.97 μ and 1.44 μ. Water shows a weak band at 1.50 μ, a strong one at 2.97 μ and one of medium intensity at 5.99 μ. The harmonic ratio between the last two bands must be regarded as accidental since the band corresponding to the greater wave-length is the less intense. It is difficult to say to what extent the occurrence of these bands having wave-lengths in harmonic ratios is accidental and to what extent they are the result of non-sinusoidal periodic vibrations. The bands are apt to be broad and the determination of wave-lengths is uncertain. A careful remeasurement of the positions of the maxima of the bands in question would be instructive. We have already remarked (footnote, p. 706) that the bands introduced into the absorption spectra of gases having more than two atoms to the molecule need not be exact harmonics of the fundamental frequencies. On the other hand it seems probable from analogy with the diatomic case that they would frequently be nearly so.

The Dependence of Frequency on the Amplitude.

In addition to destroying the simple harmonic character of the motion the lack of linearity in the relation between displacement and restoring force in the case of diatomic molecules will make the frequency a function of the amplitude of the motion. R. Seeliger[1] has recently given a discussion of the effect of terms of the second degree in the displacement on the motion of an oscillator and the energy which it emits, in which he deduces a relation between the breadth of an emission line, the magnitude of the second degree term and the rate at which energy is radiated, on the assumption that the emission of energy is in accordance with the classical electrodynamics and that the vibrators have all amplitudes between zero and a certain maximum. On this theory the width and

[1] R. Seeliger, Verh. d. D. Phys. Ges., 16, p. 1042, 1914.

position of an absorption line should depend on the temperature of the absorbing medium. But on the basis of the older form of the quantum theory for which we claim decisive evidence practically all the energy will be absorbed by molecules which originally had no vibratory energy and which after absorption have a single quantum. These molecules have a single definite frequency independent of the temperature. If the molecule can absorb two quanta of energy without splitting apart a second absorption band at a different position should begin to appear at very high temperatures. At 1,000° C. about 9 per cent. of the molecules would have one quantum and 0.8 per cent. would have two. Consequently the absorption band due to the molecules having two quanta would have an intensity of the order of magnitude of one tenth of the intensity of the band at 4.6 μ at this temperature.

POSITION OF HIGH TEMPERATURE BAND OF CARBON MONOXIDE.

A rough idea of the position of this high temperature band may be obtained from the relative intensities of the bands at 4.6 μ and 2.3 μ. An approximate solution of the equation of motion (2) may be obtained by neglecting all but the first two terms of the right-hand member. The equation then takes the form

$$m\frac{d^2z}{dt^2} = -kz - k_2z^2. \tag{6}$$

Seeliger (l. c.) gives the following approximate solution of (6).

$$z = A'\cos 2\pi\nu t + A''\cos 4\pi\nu t + \text{Const.}, \tag{7}$$

where

$$A' = A\left(1 + \frac{Ak_2}{3k_2}\right), \tag{8}$$

$$A'' = \frac{A^2k_2}{6k}, \tag{9}$$

$$\nu = \nu_0\left[1 - \tfrac{5}{12}A^2\left(\frac{K_2}{K}\right)^2\right], \tag{10}$$

$$\nu_0 = \frac{1}{2\pi}\sqrt{\frac{K}{m}}. \tag{11}$$

We assume that the waves radiated have the same form that they would have according to the classical electrodynamics if the motion of the vibrating atoms were not damped by the radiation. Let E' and E'' be the energies radiated of frequencies ν and 2ν respectively. Then

$$\frac{E'}{E''} = \frac{A'^2\nu^2}{A''^2 4\nu^2}$$

or

$$\frac{A'}{2A''} = \pm\sqrt{\frac{E'}{E''}}. \tag{12}$$

Granting that the ratio, E'/E'', of the intensities of the two emission bands can be determined from the relative intensities of the corresponding absorption bands, it is possible to compute all the constants characteristic of the motion. From (8), (9) and (12) we have

$$A' = A + 2A'' = A - A'\sqrt{\frac{E''}{E'}},$$

or,

$$A = A'\left(1 + \sqrt{\frac{E''}{E'}}\right), \tag{13}$$

if we choose the positive sign in (12). The energy is all kinetic when d^2z/dt^2 vanishes, *i. e.*, when

$$A' \cos 2\pi\nu t + 4A'' \cos 4\pi\nu t = 0.$$

Substitute the symbol x for $2\pi\nu t$ and solve the above equation for $\cos x$. Thus

$$\cos x = \frac{1}{8}\left[-\frac{A'}{2A''} \pm \sqrt{\frac{A'^2}{4A''^2} + 32}\right]$$

or

$$x = \cos^{-1}\left[\frac{1}{8}\sqrt{\frac{E'}{E''}} \pm \frac{1}{8}\sqrt{\frac{E'}{E''} + 32}\right]. \tag{14}$$

Denote the set of roots of this equation corresponding to the numerically smaller value of $\cos x$ by x_1. The total energy of the molecule is then equal to its kinetic energy when $x = x_1$, *i. e.*,

$$\begin{aligned} e = \tfrac{1}{2}m\left(\frac{dz}{dt}\right)^2_{x=x_1} &= 2m\pi^2\nu^2(A' \sin x_1 + 2A'' \sin 2x_1)^2 \\ &= 2m\pi^2\nu^2A'^2\left(\sin x_1 - \sqrt{\frac{E''}{E'}} \sin 2x_1\right)^2. \end{aligned} \tag{15}$$

We do not know what the size of a quantum is for a non-sinusoidal periodic motion but we may be reasonably sure that it must have $h\nu$ as a limit when the motion approaches the simple harmonic type. Hence $h\nu$ may be taken as an approximate value of the energy. Substituting $h\nu$ for e in (15) the equation may be solved for A' in terms of known quantities.

$$A' = \sqrt{\frac{h}{2m\nu}} \frac{1}{\pi(\sin x_1 - \sqrt{E''/E'} \sin 2x_1)}. \tag{16}$$

Having obtained the numerical value of A', the equations (12), (13), (9), (10) and (11) enable us to compute the values of k_2/k, ν_0, k and k_2 in turn.

But in order to get any of these quantities we must first obtain the value of E'/E'' from the absorption curves. The question of the relation between emission and absorption is a very difficult one. Kirchhoff's law certainly cannot hold here, for it says that the ratio of the energy emitted by a body at the temperature T in the frequency interval $d\nu$ to the coefficient of absorption for that interval is proportional to the intensity of black radiation of frequency ν. But at room temperature the intensity of black radiation at 4.6 μ is enormously greater than the corresponding intensity at 2.3 μ.[1] Consequently the ratio of the intensities of the absorption bands at 2.3 μ and at 4.6 μ would be enormously greater than the ratio of the emission bands, and the slightest departure from linearity in the law of force would produce a very strong absorption band at 2.3 μ. Such an assumption is entirely inadmissible.

In the absence of any detailed knowledge of the nature of the process of absorption we are forced to make the most plausible assumption possible regarding the ratio of the intensities of the two bands. According to the classical electrodynamics[2] the rate at which an ideal linear oscillator of frequency ν, in which the restoring force is strictly proportional to the displacement, absorbs energy is proportional to K_ν/β where K_ν is the intensity of the radiation per unit frequency which flows past it and β is the mass coefficient. Let ν' denote the fundamental frequency of the vibrations of any diatomic molecule and let ν'' denote the frequency of the first harmonic. For the present the effect of the molecular rotations will be neglected. We assume that when a beam of light of intensity K_ν and solid angle $d\Omega$ is passed through the gas each molecule will in a unit of time on the average absorb the energy $\gamma' K_{\nu'} d\Omega$ from the frequencies in the immediate neighborhood of ν' and the energy $\gamma'' K_{\nu''} d\Omega$ from the frequencies in the neighborhood of ν''. We further assume that the ratio of the molecular absorption coefficients per molecule, γ' and γ'', is equal to the ratio of the energies emitted in the corresponding emission bands, *i. e.*, that

$$\frac{\gamma'}{\gamma''} = \frac{E'}{E''}. \tag{17}$$

Let ν_r be the frequency of rotation of any given molecule. The effect of this rotation on the emission is to split the energy which would other-

[1] Let ν' and ν'' denote the frequencies corresponding to the centers of the bands at 4.6 μ and 2.3 μ respectively. Then the ratio of the corresponding intensities at 290° absolute is

$$\frac{K_{\nu'}}{K_{\nu''}} = \frac{\nu'^3}{\nu''^3} \frac{e^{\frac{h\nu''}{KT}} - 1}{e^{\frac{h\nu'}{KT}} - 1} = \frac{1}{8} \frac{e^{\frac{6,290}{290}} - 1}{e^{\frac{3,120}{290}} - 1} = 5,800.$$

[2] Cf. J. H. Jeans, Report on Radiation and the Quantum-Theory, London, 1914, pp. 12–13.

wise be radiated at the frequency ν' into two parts having the frequencies $\nu' + \nu_r$ and $\nu' - \nu_r$.[1] Similarly, radiation which would otherwise be sent out with the frequency ν'' is split up into parts having the frequencies $\nu'' + \nu_r$ and $\nu'' - \nu_r$. We will call the first pair of frequencies the effective frequencies of the fundamental and the second pair the effective frequencies of the first harmonic. The effect of the rotation on the absorption is to split the absorption lines due to the group of molecules having any given frequency of rotation into two lines having each the corresponding effective frequency. The energy absorbed by a thin layer of gas from the frequency interval $d\nu$ of a beam of intensity K_ν and solid angle $d\Omega$ is proportional to $\gamma' K_\nu d\Omega (dN/d\nu) d\nu (= \gamma' K_\nu d\Omega (dN/d\nu_r) d\nu_r)$, where $(dN/d\nu)d\nu$ is the number of molecules per unit volume having their fundamental effective frequencies in the interval $d\nu$, if that interval is close to the fundamental frequency ν_0'. If $d\nu$ is near ν_0'' the energy absorbed is proportional to $\gamma'' K_\nu d\Omega (dN/d\nu) d\nu (= \gamma'' K_\nu d\Omega (dN/d\nu_r) d\nu_r)$. The corresponding absorption coefficients are

$$\alpha' = a\gamma' \frac{dN}{d\nu_r},$$

$$\alpha'' = a\gamma'' \frac{dN}{d\nu_r},$$

α', α'' and $dN/d\nu_r$ are functions of ν_r, but for any given value of ν_r, $dN/d\nu_r$ will have the same value in the expression for α' as in that for α''. Therefore

$$\frac{\alpha'}{\alpha''} = \frac{\gamma'}{\gamma''} = \frac{E'}{E''} \tag{18}$$

if α' and α'' are measured at corresponding points of the two absorption bands.

The task of evaluating E'/E'' is then equivalent to that of finding the ratio of the absorption coefficients at corresponding points of the two curves as given by Burmeister. Owing presumably to the fact that the slit widths employed in investigating the two curves for CO did not cover equal frequency intervals, the high frequency band is somewhat more flattened than the other (cf. p. 705) and for this reason the writer has plotted the absorption coefficients as ordinates against rotation frequencies as abscissas and taken the ratio of the areas under the two curves as the measure of E'/E''. The method of computing the values of the absorption coefficients from the values of the total absorption in a finite length of tube as given by Burmeister is described in the preceding paper on "The Distribution of Angular Velocities among Diatomic Gas Molecules."

[1] Cf. introduction to preceding paper.

The computed value of E'/E'' for the two bands of carbon monoxide is 75. Hence

$$x_1 = 102° 10'.$$

The value of m computed from (1a) is

$$m = 11.25 \times 10^{-24} \text{ gm.}$$

Hence

$$A' = 6.53 \times 10^{-10} \text{ cm.},$$
$$A'' = -0.376 \times 10^{-10} \text{ cm.},$$
$$A = 7.28 \times 10^{-10} \text{ cm.},$$
$$\nu = c/\lambda = 6.44 \times 10^{13} \text{ sec.}^{-1}$$
$$\nu_0 = \nu/0.96 = 6.71 \times 10^{13} \text{ sec.}^{-1}$$

The energy will evidently be roughly proportional to A^2. Let ν' be the frequency of the molecules which have two quanta of energy. Its value may be obtained from (10) by substituting $2A^2$ for A^2. Thus

$$\nu' = \nu_0 \left[1 - \frac{10}{12} \left(\frac{A k_2}{K} \right)^2 \right] = 6.17 \times 10^{13}.$$

The corresponding wave-length is

$$\lambda' = 4.87 \, \mu.$$

The reader will observe by reference to Fig. 2 of the preceding paper that the maximum of the high temperature band comes close to the edge of the band due to the molecules which are taking up their first quantum of vibratory energy. Consequently the appearance of the former ought to be easily observable.

The Law of Interatomic Force.

It is of interest to compute the value of n in the law of force from the values of k and k_2 on the assumption that the law has the form (5). Expanding (5) in a power series in Δr we obtain

$$F(r_0 + \Delta r) = -nar_0^{-(n+1)} n \left[\Delta r - \frac{(n+1)(\Delta r)^2}{2r_0} + \cdots \right]. \quad (19)$$

Comparing with (6) we see that

$$\frac{k_2}{k} = -\frac{(n+1)}{2r_0}. \quad (20)$$

The value of r_0 computed from the separation of the maxima of the doublet at 4.66 μ is 1.10×10^{-8} cm. Also

$$\frac{k_2}{k} = \frac{6A''}{A_2} = -0.428 \times 10^9.$$

Hence

$$n = -2r_2\frac{k^2}{k} - 1 = 8.43.$$

This result is in accord with the values of n elsewhere obtained for the law of intermolecular force.

HARMONICS IN THE ABSORPTION SPECTRA OF HYDROCHLORIC ACID AND HYDROBROMIC ACID.

The absence of observable harmonics in the infra-red absorption spectra of HCl and HBr is difficult to explain. Owing to the small mass of the hydrogen atom the amplitude of the vibration should be much greater for these molecules and consequently the first harmonic should be relatively stronger than in the case of carbon monoxide. In fact, assuming that n has the value 8, the writer computes that the first harmonic in the spectrum of HCl should have an absolute intensity about three times as great as that of the first harmonic in the spectrum of CO. It is highly desirable that a careful search be made for these harmonics in the infra-red absorption spectra of HCl and HBr.

NEW EVIDENCE FOR THE OLDER FORM OF THE QUANTUM THEORY.

A consideration of the change in frequency with the amplitude gives new evidence in favor of the older form of the quantum theory which has been assumed throughout the present paper. This evidence is entirely independent of the theory advanced as to the nature of the carbon monoxide absorption band at 2.34 μ.

Assume that the law of force between the atoms of the carbon monoxide molecule is of the form (5) and give n the minimum value 5. Then k_2/k takes the value -2.73×10^8. For a molecule having one quantum of energy, A becomes 0.726×10^{-9} cm. and ν/ν_0 becomes 0.984. Hence

$$\nu - \nu_0 = 0.0164\nu_0.$$

The corresponding wave-length interval is 0.078 μ or about two thirds of the distance between the maxima of the double absorption band. (See Fig. 2 of the preceding paper.)

Now according to the later form of Planck's theory the absorbing molecules having any given rotational energy should have all vibrational energies between zero and one quantum. In fact they are assumed to be uniformly distributed over the "region element" between these extreme values of the energy. Consequently the molecules having any given rotational energy should absorb all wave-lengths between λ_0 and λ. They would give rise to a flat-topped elementary absorption band having

a width two thirds as great as the distance between the maxima of the doublet. Under such conditions these maxima could not possibly be as sharply defined as they are.

Making the same computation for the HCl molecule, the width of the elementary absorption band due to the molecules having a single angular velocity turns out to be nearly *twice* the distance between the maxima of the observed absorption band. It is only possible to conclude that the process of absorption is in some way discontinuous so that the frequency of the absorbed radiation depends only on the final energy of the absorbing oscillator.

SUMMARY.

1. The writer has attempted to show that owing to the lack of linearity in the law of force between the atoms in a diatomic molecule the infra-red absorption band due to the vibration of the atoms along their line of centers should be accompanied by a faint harmonic.

2. The absorption bands at 2.34 μ and 4.66 μ in the spectrum of carbon monoxide have been adduced as an example of such harmonics and reasons have been given for believing that the relation between their wave-lengths is not accidental.

3. It has been shown that on the basis of the same theory it is to be expected that at sufficiently high temperatures a new band should appear near the fundamental low temperature band.

4. The position of this high temperature band for CO has been roughly computed.

5. From the magnitude of the faint harmonic in the carbon monoxide spectrum it has been computed that the force between the atoms must vary inversely as the 8.5th power of the distance between their nuclei.

6. It has been shown that the sharpness of the maxima of double absorption bands in the spectra of carbon monoxide and hydrochloric acid is incompatible with the newer form of the quantum theory in which absorption is supposed to take place gradually and not by quanta.

JEFFERSON PHYSICAL LABORATORY,
HARVARD UNIVERSITY,
August 9, 1916.

ON THE IONIZATION OF GASES BY ALPHA RAYS.

By H. A. Bumstead.

IT has long been known that a metal plate struck by α-rays emits electrons, often called δ-rays, whose velocities are such as would be acquired in falling through a potential difference of a few volts. More recently it has been shown[1] that a small proportion of much swifter electrons are present among the slower ones. Velocities as high as 2.7×10^9 cm./sec. (which corresponds to a potential difference of 2,000 volts) have been observed,[2] and electrons of all speeds less than this are present in the stream from the metal. The number having any given velocity is greater as that velocity is less. It is quite plain from the experiments that many of the slower δ-electrons are produced, not directly by the α-rays, but through the intermediate agency of the swifter electrons.

It has been known too that the production of δ-rays by the α-rays is, in some respects at least, analogous to the ionization of a gas by the same agent. Thus, for example, the number of δ-electrons, due to a given pencil of α-rays, varies with the speed or range of the α-rays in the same manner as the number of ions produced in a gas, the variation being given by the well-known Bragg ionization curve.[3] In fact there are many indications that the emission of the slow δ-electrons may properly be regarded as an ionization of the metal or perhaps of a film of adsorbed gas upon its surface.

Since electrons of considerable speed exist among the δ-rays we should, from this point of view, expect to find them also when gaseous molecules are ionized by α-rays; these swifter electrons would, in their progress through the gas, cause further ionization. Thus the column of ions produced by an α-particle "would be made up of the tracks of many secondary electrons radiating irregularly from the axis of the column and extending only a small fraction of a millimeter from it";[4] it would indeed resemble the tracks of X-rays as shown in Wilson's photographs,

[1] Wertenstein, Le Radium, 9, p. 6, 1912. Bumstead and McGougan, Am. Jour. Sci., 34, p. 309, 1912; Phil. Mag., 24, p. 462, 1912.

[2] Bumstead, Am. Jour. Sci., 36, p. 107, 1913. Phil. Mag., 26, p. 250, 1913.

[3] Am. Jour. Sci., 32, p. 410, 1911. Phil. Mag., 22, p. 914, 1911.

[4] Am. Jour. Sci., 34, p. 328, 1912. Phil. Mag., 24, p. 482, 1912.

but on a very minute scale, and with the ions and the electron trails densely crowded together. But, though small compared with X-ray ionization phenomena, the α-ray columns would, on the view explained above, be considerably larger than if all the ions were formed directly by the α-particle itself. In the latter case the radius of the column at the initial instant would be of the order of the mean free path of an ion, say 10^{-5} cm. in air at atmospheric pressure; whereas if the size of the columns is due to the range of the swifter δ-electrons, we might expect initial radii of the order of 10^{-3} cm.; as may be inferred from Lenard's[1] measurements of the absorption by gases of cathode rays whose speeds correspond to 1,000 and 4,000 volts.

So great a difference in the diameter of the columns would cause a very marked difference in the amount of initial recombination to be expected on the two hypotheses. Professor Wellisch and Dr. Woodrow[2] were good enough to investigate this point for me in the course of some experiments on columnar ionization, and their calculation gave for the initial radius of the column 1.6×10^{-3} cm. They were inclined however to attribute this large value to an extremely rapid lateral diffusion of the ions which is practically over before the ions have had time to move sensibly under the action of the electric field.

Soon afterward Jaffé[3] published an elaborate mathematical investigation of columnar ionization in which the effect of diffusion in the column is taken into account. The theory thus developed is compared with experimental results obtained by Moulin, Wheelock and the author himself, and the agreement seems to be satisfactory.[4] Jaffé calculates the mean distance of the ions from the axis of the column at the time zero (*i. e.*, before diffusion has begun) and obtains[5] 1.39×10^{-3} cm. He explains this unexpectedly large value as the result of a rapid preliminary diffusion, before the electrons and positive ions have obtained their normal "loads" and therefore before his equations, with normal values of mobilities, diffusion constants, etc., begin to apply. The "initial state" of his theory is thus later than the formation of the column; and the interval between these events must be supposed to be sufficiently long to permit the column to increase its diameter approximately a hundredfold. Jaffé mentions the possibility of explaining the large diameter of the columns by the hypothesis that the α-rays produce

[1] Lenard, Ann. der Phys., 12, p. 732, 1903. J. J. Thomson, Cond. through Gases, 2d ed., p. 381.

[2] Am. Jour. Sci., 36, p. 229, 1913. Phil. Mag., 26, pp. 526 et seq., 1913.

[3] Ann. der Phys., 42, p. 303, 1913.

[4] See also Jaffé, Phys. Zeits., 15, p. 353, 1914.

[5] Ann. der Phys., loc. cit., p. 341.

primary δ-rays and that these latter ionize the gas; he rejects this explanation however "since nothing is known of δ-rays of such a kind."

Even with the knowledge of the existence of the swift δ-rays, it is not easy to arrange an ionization experiment which will show in an unambiguous manner whether or not an appreciable fraction of the ions are produced by them; the large value of the initial diameter of the columns obtained by Wellisch and Woodrow and by Jaffé certainly supports this view, but, as we have seen, it may be interpreted as due to other causes. To avoid this possibility of ambiguity in attempting to decide the question I had recourse to C. T. R. Wilson's method of photographing the tracks of α-rays in a supersaturated gas.[1] At atmospheric pressure, even in hydrogen, the diameter of the columns is so small and there are so many ions in a given length that no details of the structure of the columns could be observed. It was therefore necessary to work at reduced pressures.

The expansion apparatus used was that made by the Cambridge Scientific Instrument Co. after Wilson's design. It worked very satisfactorily with initial pressures in the expansion chamber greater than 200 mm. When however the pressure was lowered still further the expansive force of the gas became too small to push the piston down with sufficient promptness. The apparatus was therefore modified to the form shown in Fig. 1, in which the method of causing the expansion

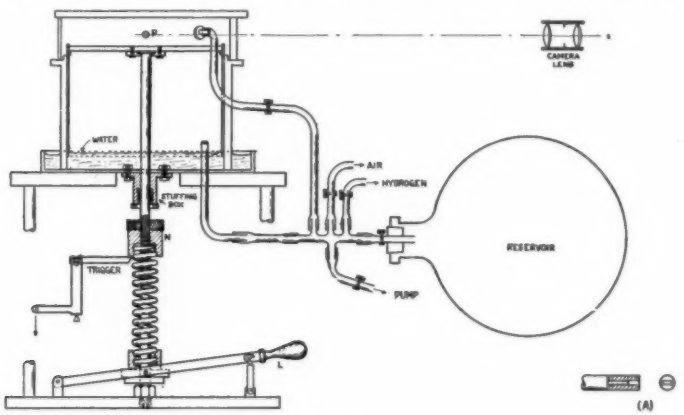


Fig. 1.

is sufficiently obvious. The nut, N, permitted the initial height of the piston to be adjusted so that any desired expansion-ratio could be obtained. The expansion chamber, the space below the piston, and the reservoir, were all filled with air or hydrogen, as the case might be, at the

[1] Proc. Roy. Soc., 87, p. 277, 1912.

desired initial pressure; the purpose of the reservoir (a two-gallon bottle) was to prevent the gas under the piston from attaining a sufficiently high pressure after the expansion to cause an appreciable leak into the expansion chamber around the piston.

It was scarcely practicable and did not seem necessary to have the hydrogen fillings very pure. The entire space to be filled was exhausted with a filter pump to about 20 mm. and hydrogen was then admitted to atmospheric pressure. This process was repeated three or four times, and the hydrogen was finally pumped down to the experimental pressure, usually between 90 and 100 mm. The hydrogen was made by the action of hydrochloric acid upon zinc and was freed from hydrogen sulphide by passing it through a solution of lead acetate.

The position of the source of α-rays is indicated at P. Polonium was deposited upon the end of a little rectangular bar of copper 2 mm. $\times$ 1 mm. in section; to "canalize" the rays a piece of brass with a rectangular channel cut in it was slipped over the copper bar as indicated at (A), Fig. 1. A small vertical piece of brass was attached to the piston so as to cover the source of α-rays except when the piston was nearly in its lowest position. In this way the rays were prevented from crossing the chamber until the expansion was nearly completed. This made it unnecessary to use an electric field in the chamber to clear away ions formed before the expansion.

With this apparatus expansions could be made at any pressures, but there was a limit below which condensation on the ions did not take place readily. In hydrogen this limiting pressure (measured before the expansion) was about 70 mm.; in air, tracks could sometimes be seen when an expansion was made from an initial pressure of 40 mm. In most of the experiments, initial pressures of 90 to 100 mm. were used; the expansion-ratio which gave the best results at these pressures was from 1.35 to 1.40.

Wilson's methods were closely followed in making the photographs. The source of light was a spark in mercury vapor contained in a narrow quartz tube; large Leyden jars charged by a Holtz machine were discharged through two such spark gaps in series. These were arranged on opposite sides of the expansion chamber and a little above it; the light passed obliquely through the top and the tracks were photographed through a plate glass window in the side of the chamber. The light from the sparks was concentrated by large condensing lenses upon the region in the chamber through which the α-rays passed. The sparks were made to occur at definite times after the expansion by means of a falling weight as described in Wilson's paper.

H. A. BUMSTEAD.

A Dallmeyer lens of approximately 35 cm. focal length was used with its full aperture, 4 cm. It was mounted on the front of a long copying camera and focused so as to give a magnification of about 1.5.

Many difficulties were encountered not all of which need be detailed here. Considerably more light is needed than for photographing α-ray tracks at ordinary pressures; it was only under favorable weather conditions and with Holtz machine, jars and spark gaps working perfectly that fairly good pictures could be obtained. Precautions had to be taken to prevent brushing as far as possible in all parts of the electric circuit. Although the α-rays were partially canalized, the fan-shaped sheaf had a considerable depth in the line of sight and many of the tracks photographed were out of focus. At the low pressures used, the diffusion of the ions is rapid so that only the rays which passed through the gas after the requisite degree of supersaturation was attained could possibly show any structure. Even after condensation the droplets were sufficiently mobile to make it necessary to illuminate very promptly after the track was formed; and often no ray crossed the field in this brief interval. On the other hand it was undesirable to use a very active source since the water vapor was exhausted and the picture confused by the older and more or less diffuse trails. Much patience and many plates had to be expended in repeated trials before satisfactory results were obtained.

Fig. 2 contains reproductions of negatives obtained in this way.[1] They could doubtless be much improved by a sufficient expenditure of time and labor. But they show with sufficient distinctness (at least in the original negatives) projections from the main trail which resemble in all respects the ends of β-ray trails as observed by Wilson. It does not seem possible that diffusion of the ions could produce columns of this appearance.

Wilson's photographs of X-ray beams make it reasonable to suppose that all the β-ray trails are of approximately equal length when due allowance is made for the foreshortening of oblique trails; this impression is strengthened on looking at the beautiful stereoscopic pictures which were exhibited by Mr. Wilson about two years and a half ago at a meeting of the London Physical Society held in Cambridge. This equality was of course to be expected from the known fact that homogeneous X-rays give rise to secondary electronic rays of a definite velocity. There is however no reason to expect a similar result with the α-rays; my own experiments on δ-rays from metals have shown that electrons of all

[1] The vertical "smudge" on each of the photographs is due to an imperfection of the window of the expansion chamber caused by scraping off some dried alcoholic shellac which had been accidently allowed to flow on it in the process of cementing it on.

velocities up to 2,000 volts are present, and there is no reason to doubt that this upper limit would have been exceeded if a sufficiently strong source of α-rays had been available. The photographs are in complete accord with these facts. Only exceptional electrons start with sufficient velocity to get clear of the crowd and form distinct β-ray trails; a larger number have smaller velocities, but still great enough to produce distinct knobs and projections from the main track; and I think there is little reason to doubt that the ragged edges of these tracks are caused in the same manner by δ-electrons of still smaller velocities.

RESULTS.

Photographs of α-ray tracks in hydrogen at a pressure (before expansion) of 90–100 mm. have been obtained by a slight modification of C. T. R. Wilson's method. They show distinct evidence of the existence of electronic trails radiating from the column, due doubtless to ionization of the gas by swift δ-rays. Such swift rays are known to be produced when metals are struck by α-rays but their existence in the process of gas-ionization by α-rays though suspected has not previously been demonstrated.

The photographs give decided support to the view that a considerable part of the ionization in the α-ray column is produced in this indirect way. The large values of the initial diameter of the columns which have been deduced from experiments on recombination find thus a ready explanation.

THE MAGNETIC PROPERTIES OF HEMATITE.[1]

BY T. TOWNSEND SMITH.

THE magnetic properties of crystals have interested many physicists since the early investigations of Plücker and Faraday, and for materials where one deals with paramagnetism or diamagnetism only, the magnetic behavior is dependent in a rather simple way upon the direction that is taken in the crystal. The treatment of this case usually passes under the name of Thomson's Theory, being due fundamentally to Sir William Thomson, though Poisson had previously noted the possibility of a dependence of the magnetic state of a crystal upon the structure of the material.

It may be shown that there are three principal directions in general in a crystal, along which the magnetization and the magnetizing field are similarly directed, and that, in the case treated by Sir William Thomson,[2] the magnetization in any other direction with a given field may be simply determined from the direction of the field and the susceptibilities along these three directions, using them as the axes in a system of rectangular coördinates. König,[3] Stenger,[4] and Tumlirz[5] attempted to put the theory to experimental test by swinging spheres of calcite and quartz in a uniform field and measuring the period of oscillation, with fair success. There have been also many determinations made of the magnetic constants along the axes of symmetry. A somewhat recent series of determinations of such constants is that of Voigt & Kinoshita,[6] in which the forces acting on the specimens in a non-uniform field were used to determine the susceptibility in these directions. There is a rather extended review of such work in Professor Voigt's Lehrbuch der Kristallphysik.[7]

When one turns to crystals in which the field is not proportional to

[1] This work was begun in the Jefferson Physical Laboratory of Harvard University, where almost all of the necessary apparatus was made and where some of the readings were taken. The work is being continued at the University of Kansas.

[2] Phil. Mag., March, 1851. Papers on Electrostatics and Magnetism, page 471.

[3] Annalen der Physik, 31: 273, 1887.

[4] Annalen der Physik, 20: 304, 1883; 35: 331, 1888.

[5] Annalen der Physik, 27: 133, 1886.

[6] Göttingen Nachr., 1907, p. 123. Annalen der Physik, 24: 492, 1907.

[7] Chapter VI., Section 5.

the resultant intensity of magnetization, one finds that the observations are not numerous and that the phenomena are complex. Professor P. Weiss,[1] of Zurich, has done more work with such material than anyone else and he, either alone or in collaboration, has published results of measurements made on magnetite and on pyrrhotite (magnetic pyrites). On hematite, which is much less strongly magnetic than either of the two just mentioned, there is some work by Westman[2] and by Jakob Kunz,[3] and likewise by Bavink,[4] who also experimented with tourmalin, garnet, and ilmenite.

The present investigation has to do with hematite, all the tests made being of the component of magnetization parallel to the exciting field. The field strengths used run as high as 3,800 gausses, within which range there is no approach to saturation, either in or perpendicular to the basal plane (plane of symmetry) of the crystal.

The quantity measured in every case was the force which pulled the specimen, a sphere, into the magnetic field, and from this force one may calculate an average intensity of magnetization for the sphere. If the susceptibility is constant throughout a spherical specimen, then to a first approximation the intensity of magnetization calculated from the pull is the value of the intensity at the center of the sphere.

This average value is the value that is given throughout the work below, though in general in hematite the susceptibility will vary, the variation being appreciable in some cases within the range of the fields that exist in the specimen. This is a drawback to the method here used. The non-uniform field is an advantage, however, in that it is possible by its use to test experimentally the homogeneity of the specimen. This may be done by the simple operation of inverting the sphere with reference to the field, in which case the pull will remain unchanged only if the upper and the lower half of the sphere are alike. Within the limits of accuracy of this test, all the specimens showed themselves to be homogeneous.

THE SPECIMENS INVESTIGATED.

Hematite crystallizes in rhombohedral crystals, with an axis of three-fold symmetry, perpendicular to a plane of symmetry, which is sometimes called the principal plane of the crystal. The crystals are opaque,

[1] Magnetite: C. R., 122: 1405, 1896; Journal de Physique, Ser. III., 5: 435, 1896; L'Eclairage Electrique, 7: 487, 1896; 8: 56, 105, 1896; Thesis, Paris, 1896; Annalen der Physik, 30: 389, 1909 (Quittner). Pyrrhotite: Journal de Physique, Ser. IV., 4: 468, 829, 1905.

[2] Upsala Universitets Årsskrift, 1896.

[3] Neues Jahrbuch für Mineralogie, 1907, Vol. 1, p. 62.

[4] Neues Jahrbuch für Mineralogie, beil. B, 19: 377, 1904.

black in color on the ground faces, but optically uniaxial, according to Foersterling[1] and others. The crystals are hard and rather heavy, density about 5.25 with good crystals, and contain no water of crystallization.

Crystal clusters are obtained from the Isle of Elba, with beautifully polished faces, which usually give several images when examined with a goniometer by reflected light. In Fig. 1 are shown several individuals, all of which were obtained from the same cluster and from which the spheres A_1, A_2, A_3, and A_4, referred to below, were cut. The beauty of the faces in a way is deceitful, for, if one of these individuals of a group be cut into, the chances are that the material will be homogeneous for only a short distance back of the faces, being pitted and non-homogeneous a little distance back. The material used in this work was obtained by sawing up the individual crystal units, and grinding until none of the ground faces showed any evidence of cracks or pits, when the piece was assumed to be homogeneous. The results of the tests made on spheres ground from such pieces have shown the specimens so selected to be many of them homogeneous, and a large part of the measurements that I have made have been upon such spheres.

A_1 was cut purposely from the part of the material back of the clean faces, where the material was pitted and evidently not homogeneous. On test it showed, as was expected, that it was not hematite, having a susceptibility much above that of the other selected specimens and a density likewise far different. The specimens A_2 and A_4 are alike, but the specimen A_3 is not at all like any of the others, showing with a low density a very high ratio between the susceptibility along and perpendicular to the axis (0.50 at a field strength of about 1,200 gausses). The most rigorous tests that I have been able to make, however, show no lack of homogeneity. The susceptibility here is also abnormally high and the hysteresis is apparently not great. The density determination was not very accurately made, because of the small size of the sphere and the variations from a true sphere, which are proportionately considerable, so that the lower density referred to above is not to be greatly relied upon.

In addition to the Elba hematite the following specimens have been used in my work:

F, a twin, from Dognacska, Hungary,
G from Ouropreto, Brazil,
J from Schabry, Ural Mountains.

[1] Foersterling, Neues Jahrb. f. Mineralogie, beil. B, 25: 344, 1908. Senarmont, Ann. de chim. et de phys. (III.), 20: 445, 1847.

In Fig. 1 are shown photographs of *F* and *J*. Some of the angles for these two, which were particularly good specimens, were measured on a two-circle goniometer and the angles between the faces were found to be generally within a few minutes of those given by Dana.[1]

For the specimen *F* all the faces, except the striated "*r*" (rhombohedral) faces, were large and bright and with reflected light gave clear images, double, with only two or three minutes separating them. The "*r*" faces were all striated and gave one bright image with an indistinct band, perpendicular to the parallel edges of the faces. The face "*c*" (basal plane) was slightly pyramidal, rising in regular steps. The crystal was broken off on one edge and the better half is shown, but the lower half exhibited several well-marked faces. The crystal measured just under two centimeters at the widest part.

For the crystal *J* the striations on the faces "*r*," one of which is here the large irregular face on the left, were rounded, giving a flash of light as the crystal was rotated on the goniometer about an axis in the plane of symmetry and a long streak as it was rotated about a normal to this plane as an axis. An image by reflection was distinguishable, but blurred, and several streaky images from each "*r*" face were obtained by reflecting sunlight against the wall of the room. These faces were heavily striated, as the figure shows, but there was not the slightest trace of fracture or cracks parallel to these striations nor did the material give such an indication when it was sawn into. Specimens cut from the crystal showed also the magnetic behavior that was to be expected from homogeneous material. The "*c*" face, the basal plane, just to the right of "*r*," triangular and pyramidal, gave two distinct images in the goniometer 3.5 minutes apart.

The specimen *G* was a large flat plate, showing fine lines of parting across the two "*c*" faces, one set parallel to one of the "*r*" faces and another less distinct set crossing the first at an angle of about sixty degrees. A specimen was cut from this crystal in the part where the lines of parting were finest and least evident, the sawn and ground faces appearing clean and smooth, and the sphere ground from this piece is the one referred to as *G* below. The faces of these plates were not true enough to give images on reflection, though they were smooth and flat.

The values of the constants for all of the spheres are given below:

THE METHOD OF EXPERIMENTING.

An expression for the force exerted upon a small, inductively magnetized sphere (*S*) in a non-uniform magnetic field has been worked out

[1] Dana, System of Mineralogy.

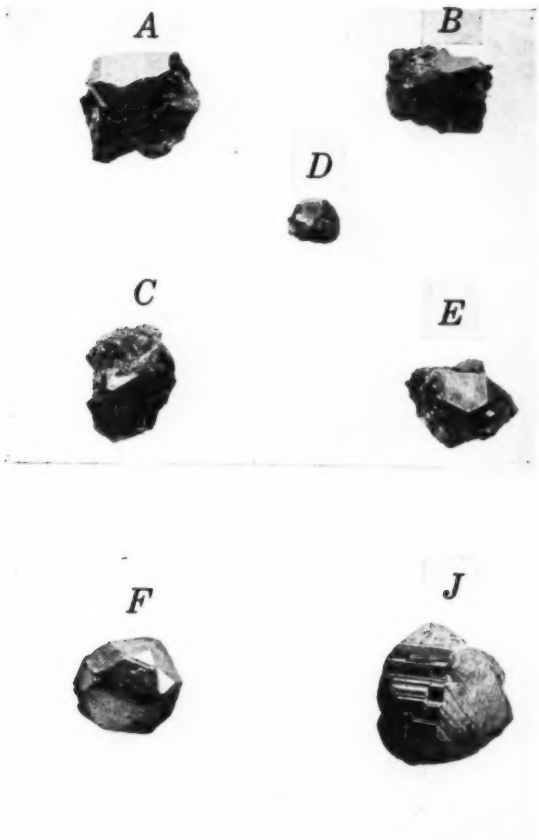


FIG. 1. Hematite Crystals. *A–E*, Isle of Elba; *F*, Dognacska, Hungary; *J*, Schabry, Ural Mountains.

T. TOWNSEND SMITH.

Spheres used in the Magnetic Measurements.

Mark.	Source.	Characteristics.	Density.	Diameter.	Volume
				cm.	c.c.
3	Elba	"Clusters" of single crystals set in an uncrystallized bed.	5.22	0.447	0.0468
5	"		5.23	0.341	0.0208
9	"		5.26	1.010	0.540
12	"		5.29	0.547	0.0857
10	"		5.26	0.683	0.1668
A_1	Elba	All from the same cluster—A_1, pitted.	4.90	0.581	0.1027
A_2	"		5.29	0.457	0.0500
A_3	"		5.22	0.408	0.0356
A_4	"		5.27	0.367	0.0259
F	Dognacska, Hungary	Twin, a large well formed crystal—see Fig. 1.	5.23	0.578	0.1011
G	Ouropreto, Brazil	Plate with fine striations, forming lines of parting.	5.23	0.593	0.1092
J_1	Schabry	Fair single crystal, striations on "c"	5.23	0.364	0.0253
J_2	Urals	and "r," but no cracks.	5.23	0.345	0.0215

by Sir William Thomson,[1] the work being based directly upon the definitions of the magnetic units. The expression for the force exerted along the y-axis has the value

$$F_y = \left[I_x \frac{\partial H_x}{\partial y} + I_y \frac{\partial H_y}{\partial y} + I_z \frac{\partial H_z}{\partial y} \right] v,$$

where F, I, and H represent respectively the mechanical force, the intensity of magnetization, and the magnetic field strength, and v is the volume of the element in question.

If one assumes that the magnetization lies in the xy-plane the last term will drop out and, if the direction of the x-axis be taken as that of the field at the center of the sphere, the second term will have a very small value, so that the final simplified result becomes

$$F_y = I_x \frac{\partial H_x}{\partial y} v.$$

The magnet used in most of the work was an electromagnet, with cylindrically shaped pole pieces, hung poles down, and the spheres were placed about level with the lower edge of the pole pieces, as is shown in the upper left-hand sketch of Fig. 2, which is roughly to scale. For adjusting purposes the spheres were cemented to wooden rods by a cement called Cæmentium, which held firmly enough for the work, and which on test proved not to be sufficiently magnetic to cause an observable difference in any of the readings.

[1] Papers on Electrostatics and Magnetism, sections 500, 638, 639.

Cylindrical pole pieces were used because it was found that with such pole pieces the field gradient was very nearly constant over a considerable range, and this is desirable. The pole pieces shown in the sketch have a radius of curvature of about seven centimeters, a depth of a little over three, and a height of about two and a half centimeters, and, where the jaws come closest together at the top, they are separated about seven

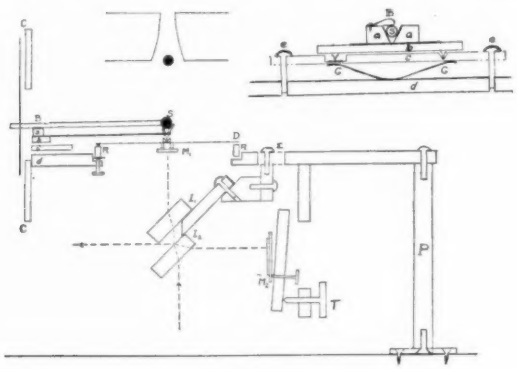


Fig. 2.

The Mounting of the Specimen.

millimeters by a brass plug. The other pole pieces, which were used for lower fields in some cases and with which all the measurements for sphere 9 were taken, are somewhat larger and are separated by a somewhat wider plug.

The field strength was determined by jerking out of the field a narrow exploring coil of thirty turns with an equivalent area of about 6.48 square centimeters. The coil, attached to a light wooden strip, was thrown something like a foot from the point where the field strength was to be determined, and on test the field strength in the neighborhood of the thrown coil was shown to be negligible. The field gradient was determined from the galvanometer deflection obtained by pulling a flat wooden plug from under the exploring coil.

In taking readings of the force a sphere was placed in a little glass cup, which bore upon the center of a three-inch disk of cover glass. The bending of the cover glass, as the field was gradually put on and the weight of the sphere was in part balanced by the force due to the magnetic field, was measured by the shifting of the fringes in a Michelson interferometer arrangement, one mirror of which was attached to the center of the cover glass disk. Fig. 2 shows the arrangement of the interferometer.

I_1 and I_2 are the interferometer plates, M_1 and M_2 the interferometer

mirrors. The coarse adjustment of distances is made by moving the plates, the fine adjustment by moving the mirror M_2, by means of three thumbscrews (only one of which is shown) and a swinging plate, which is controlled by the thumbscrew T. There is a flat spring to hold M_2 against the three thumbscrews on which it bears, and two others hold the swinging plate against T.

The somewhat complicated mounting of the disk and specimen appeared to be the simplest way of meeting the experimental requirements, which are that the fringes be steady at all times, that the specimen and mounting be readily removable, and that the specimen be free to rotate so that different directions in the crystal may be in succession made to take the direction of the magnetic field. The disk D is cemented to a glass ring RR at three points, where small glass beads are used to separate the two, and this ring rests upon three thumbscrews in the base plate of the apparatus by a point, groove and plane support. The cement keeps D from slipping, as it otherwise always would, and the whole mounting is readily removable when occasion arises for changing disks. To the disk at its center a small cone-bored jewel bearing is cemented with a trace of cement, and this jewel supports the carriage that bears the sphere under investigation. If the cup, in which the sphere rests, is cemented directly to the disk D, any torque that may be exerted upon the sphere makes its presence felt by a twisting and distortion of the fringes.

The construction of the carriage that bears the specimen is shown in the two sections that are given in the figure. The hematite sphere S is cemented to a wooden rod and the two are supported by the glass cup referred to above and the two wooden blocks aa. B is a small spring of brush copper that by friction keeps the sphere from turning under the influence of the small couples of the magnetic field. The blocks and the cup are cemented to a strip of cover glass which is in turn supported by three points, of which one rests in the jewel bearing on D and the other two are cemented to the glass strip b and rest upon the glass faced groove and plane cut in the brass plate c above GG. The German-silver spring GG holds the plate c up against the adjusting screws ee, by which the plate may be raised or lowered, and these screws pass through slots that make possible a right and left adjustment of the plate c. These adjustments, together with vertical slots in the plate CC, permit the rod BS to be levelled and at the same time to be brought to the center of the divided circle that is marked on CC. A glass pointer enables one to read angles on this circle, as the sphere is rotated about the axis BS.

The force acting on the sphere in dynes was calculated from the deflec-

tion produced, measured in fringes. For calibration a light, German-silver, spiral spring was mounted on a windlass arrangement that could be screwed to the brass bed plate and the windlass on being turned stretched the spring by a known amount. There was no external pull acting on the windlass at the beginning or end of the stretching, except the weight of some twenty centimeters of very light twine, which was used to turn the windlass between fixed stops. The spring was calibrated with light wire weights and a microscope cathetometer. With the disk used in most of the work, a deflection of one fringe would be produced by a force of about twelve dynes.

PRELIMINARY TESTS OF THE SPHERES.

In the earlier work the spheres were stuck on to the wooden rods in a random position with a bit of Cæmentium and then placed on the interferometer, readings of the pull being taken for a number of angles in the zone perpendicular to the rod. The readings were plotted and the maximum determined from the plot, which can be rather accurately done—within probably less than two degrees—if the zone is somewhat removed from the principal plane. Using this maximum for the axis of rotation, a new zone, perpendicular to the first one, is obtained, which should contain the direction of the axis of symmetry of the crystal. This could be tested by resetting with the maximum of this zone for an axis of rotation and getting a third zone, perpendicular to the second, which should likewise contain the axis of symmetry, or the magnet could be rotated a few degrees and thus readings for the neighborhood of the minimum obtained without remounting. Tested in both ways, all of the spheres for which the constants are given in the table above were found to possess a true minimum. Most of the specimens were remounted with this minimum as an axis of rotation, and within the accuracy of the work all the spheres so tested showed no dependence of magnetization upon direction in this zone.

The direction of the maximum may be somewhat more quickly obtained by hanging the sphere, mounted at random, in a magnetic field—a horseshoe magnet is sufficient—and then the direction of the maximum and that of the field should coincide. One obtains the axial zone by using this direction as the axis of a second zone.

THE TWO TYPES OF CRYSTALS.

The specimens that I have tested may be divided into two general classes—those which exhibit no signs of hysteresis and show an intensity of magnetization proportional to the field in the direction of the axis of

symmetry, and another group in which the hysteresis phenomena along the axis are particularly marked. In the first of these two classes, the specimens are paramagnetic along the principal axis and ferromagnetic, that is, exhibit hysteresis, in the principal plane of the crystal; in the second the specimens (all of Elba hematite) are ferromagnetic in all directions, the intensity in the direction of the principal axis being considerably more than for the first group, and the intensity in the principal plane in all observed cases, with the possible exception of A_3, being noticeably less. There is no difference in the appearance of the specimens, though the density of the first group is apparently a bit lower than is the case with the second. A chemical analysis should be made, but such an analysis would be inconclusive unless made on tested specimens, because spheres cut from crystals from the Island of Elba will be found in both groups. I have specimens from Elba, cut from the beautiful clusters which that district provides, that exhibit magnetic properties which are indistinguishable from those exhibited by a sphere cut from a flat plate of Brazilian hematite (G), and by spheres cut from J, which comes from the Ural Mountains and is a specimen very similar in appearance to some of the Elba crystals.

The crystals of the first group are represented by spheres 3, 4, 5, F, G, J_1, J_2: those of the second group by 9, 12, A_2, A_4. I have tested a number of other spheres of Elba hematite, most of which would probably belong in group two, though I am somewhat doubtful in several cases as to the homogeneity of the crystals.

In some old tests of Rammelsberg[1] on Elba hematite, he speaks of two sets of crystals, one with a density of 5.241 and the other of 5.283 grams per cubic centimeter, which differed only slightly in composition. The heavier specimens contained just under one half of one per cent. of talc earth, and a trace of silicic acid, while the lighter specimens showed traces of both titanic and silicic acids. Both contained a little ferrous iron.

THE CRYSTALS AXIALLY PARAMAGNETIC.

Among the crystals of this group spheres 3 and 5, from Elba hematite, sphere G, from Ouropreto, Brazil, and spheres J_1 and J_2, from the Ural Mountains, are almost indistinguishable in their magnetic properties, though the greater size of G makes the measurements on this sphere more reliable than those on the others. The sphere F (twin), from Dognacska, Hungary, shows an intensity well above that of any of the other specimens of this group. All of them exhibit a magnetization parallel to the axis that is proportional to the field within the accuracy

[1] Annalen der Physik, 104: 528, 1858.

of the measurements made. The magnetization curves for spheres *G* and *F* are given in Fig. 3, both along the axis and in the principal plane.

It was necessary to take the readings in sections with different choices of disks, pole pieces, and magnets for each region of magnetic field strength, because even though the value of the magnetic intensity may

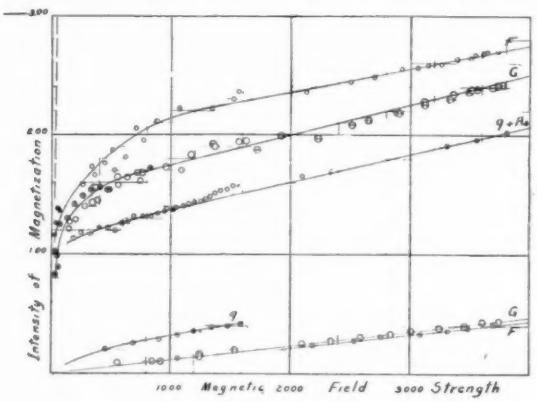


Fig. 3.

Magnetization Curves for Hematite. The upper curves in each case show the intensity of magnetization in the principal plane of the crystal, and the lower curves the intensity along the axis. The broken line indicates the correction that is to be made to the field strength to take into account the demagnetizing action of the sphere.

be changing only slowly, the force exerted upon the specimen and the fringe shift both mount rapidly as the field increases. With a constant susceptibility the force exerted increases nearly in proportion to the square of the field strength, if, as was the case, the field gradient is nearly proportional to the field, and with a hard magnetized body the increase would be in proportion to the field strength, for the force is given by the expression

$$F = I \cdot G \cdot v.$$

where *G* is the field gradient.

All of the readings for fields above about 1,600 gausses were taken with the pole pieces No. 1 mounted on a large magnet in the laboratory of the physics department of the University of Kansas, while the readings for field strengths below this were made with both sets of pole pieces on a smaller electromagnet with which the majority of my determinations have been made. The readings for values of the field below seventy-five gausses were made with the use of a permanent horseshoe magnet and a Becker balance.

The concordance of the results is not all that could be desired, but considering the variety of circumstances under which the different

readings were made, I was somewhat surprised to see the different ranges run into one another so well. In Fig. 3 the points obtained for sphere *G* with the large magnet are shown by the barred circles, the different sets of readings obtained with the smaller electromagnet are differentiated in the plotting, the most reliable probably being the crossed circles. The points for sphere *F*, indicated by smaller circles, represent similarly several distinct sets of readings.

The points determined with the permanent magnet are indicated with an *x* in the circle. The higher of these readings are probably a bit too high, a correction that was made for a rapidly changing gradient being probably too small.

All of the readings taken in the several runs are shown with the exception of a group of five for the sphere *F*, all of them representing a fringe movement of 1.1 fringes and less, and all of them lying appreciably lower than would appear possible from the readings taken with the permanent magnet. These I have thought it legitimate to discard. The values for spheres 3, 5, J_1, and J_2 would lie in good agreement with those for *G*.

The curves represent a case of ferromagnetism with very low intensities, in which there is no sign of approaching saturation at comparatively high fields.[1] The curves show likewise that the intensity of magnetization must change very rapidly with the field for weak fields.[2]

With the spheres of this first group the amount of hysteresis is relatively small. The forces exerted in non-uniform fields are slightly greater with decreasing than with increasing fields, but the difference is very slight.

For the direction of the axis of symmetry of the crystal the values of the intensity of magnetization are proportional to the field strengths, as is shown by the following figures showing a run for the sphere *G*:

Field	2,100	2,340	2,590	2,840	3,010	3,250	3,460	3,610	3,750
Intensity	.247	.272	.302	.328	.360	.384	.398	.430	.441
Susceptibility	.118	.116	.117	.115	.120	.118	.115	.119	.118
Mean value									$.117\times10^{-3}$

These values are plotted in Fig. 3, together with four others made at lower fields. A similar set of determinations made on the sphere *F* gave:

Field	2,190	2,540	2,760	3,090	3,320	3,490	3,700
Intensity	.238	.271	.307	.329	.357	.382	.407
Susceptibility	.109	.107	.111	.106	.108	.109	.110
Mean value							$.109\times10^{-3}$

[1] P. Weiss, loc. cit. B. O. Peirce, Am. Jour. Sci., 27: 293, 1909.

[2] J. Westman, loc. cit.

These values are more accurate than similar figures for spheres 3 and J_1, J_1 showing a result equal to that for G, within the experimental error, and 3 giving a result that is apparently a little lower, though again probably within the experimental error of the determinations. In both these latter cases is the calculated intensity nearly proportional to the field strength within the range from about 1,800 to about 4,000 gausses.

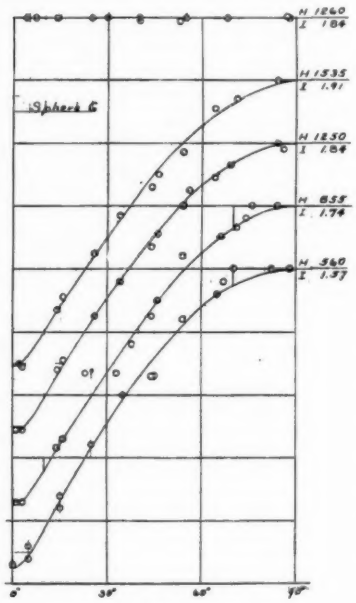


Fig. 4.

Intensity of Magnetization in the Axial Zone for Sphere G. The ordinates give the intensity of magnetization, in terms of the maximum for the zone, the value of which is taken as one. The curves are displaced vertically to avoid confusion. The points above show a zone that is very nearly perpendicular to the axis.

In Fig. 4 are shown plots of the forces exerted upon sphere G for directions which lie between the principal plane and the axis of symmetry and for which the direction of magnetization does not coincide with the field, and similar curves could be given for spheres F, 3, 4, and 5. Fig. 4 shows the points for an axial zone for sphere G all plotted in one quadrant, though the readings here represented were taken throughout the whole circumference. The top curve in the figure represents readings taken in the principal plane, nearly, and it is evident that there is no evidence of three-fold symmetry. The constancy here indicated of the component of the intensity parallel to the field has been remarked by Kunz,[1] using specimens of Vesuvian hematite in the shape of disks with faces parallel to the principal plane.

The set of curves for G shows how slowly the shape of these curves, which represent the intensity parallel to the field, changes with the field strength. Except for a small range near the minimum, one could use the same form for drawing all the curves and get an agreement lying within a probable experimental error, which is relatively larger with weaker fields. The values given for the intensity I are for the principal plane—the intensities in other directions are plotted as fractional parts of the maximum in Fig. 4.

The values plotted to rectangular coördinates in Fig. 4 for a field of 1,250 gausses are shown in Fig. 5 plotted to polar coördinates. A plot

[1] Loc. cit.

of this sort, however, does not represent the changes in intensity near the minimum as well as a plot with rectangular coördinates, so that I have used these latter in all the other plots where angles are involved.

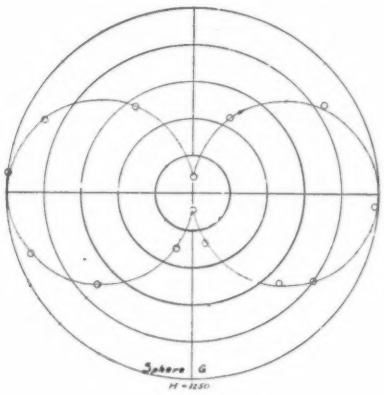


Fig. 5.

The Values of One of the Curves of Fig. 4 Plotted to Polar Coördinates. Field strength 1,250 gausses.

THE AXIALLY FERROMAGNETIC CRYSTALS.

The curves of Figs. 6 and 7 represent attempts to obtain hysteresis curves for sphere 9, made before I quite appreciated the difficulty that would arise in interpreting the results of the observations. The lower curve of Fig. 6 represents the forces exerted in fields running up to 700

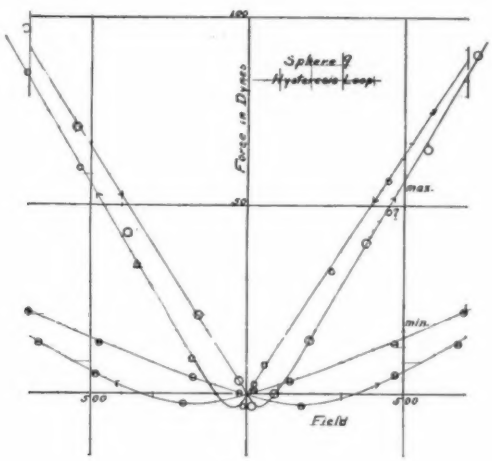


Fig. 6.

The Force Acting on Sphere 9 with Changing Field. Upper curves, direction of the field in the principal plane of the crystal. Lower curves, direction of the field parallel to the axis of the crystal. The curves would close if produced to the maximum field strength, 1,500 gausses.

gausses upon the sphere when the axis was directed along the direction of the magnetic field and the field was gradually run through a complete cycle, starting from a value near the maximum. The curves, produced, are closed curves at the maximum fields used, about 1,500. The values are corrected slightly for a slow fringe shift, due probably to slow temperature changes in the room, which does not affect the evidence of hysteresis, for this lies in the difference between the two curves for increasing and for decreasing fields. The similar curve for the direction of the principal plane is shown also in Fig. 6, drawn to the same scale as

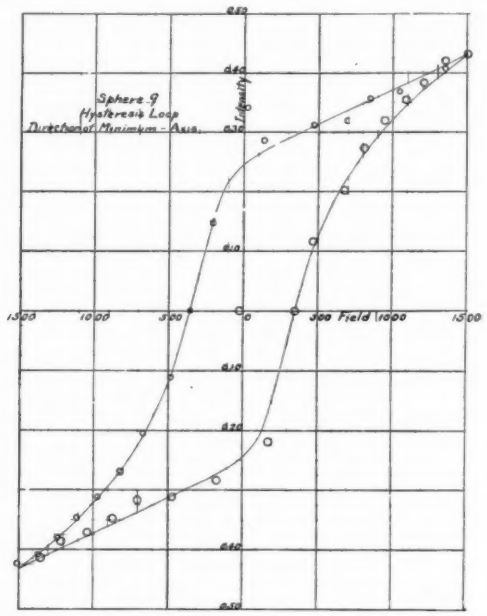


Fig. 7.

Hysteresis Loop for Sphere 9 (Elba). The direction of the field is parallel to the axis of the crystal, and the values of the intensity are calculated from the forces, which are shown in the lower curves of Fig. 6.

for the direction of the axis. Here as before the hysteresis is in evidence, but the difference between the ascending and the descending limbs is less marked.

Both of these curves involve, of course, the field gradient, and I have calculated and plotted the values of the intensity, which are shown for the minimum in Fig. 7. The values on the descending arm for low field strengths are very uncertain. For the maximum direction the curve of the intensity would be similar, though not so pronounced in character. For this direction the readings that I have are not accurate enough to bear translation into an *HI* curve.

The high coercive force shown in the figure for the direction of minimum magnetization was otherwise made evident when I hung the sphere 9 by a silk thread between the jaws of a permanent magnet where the magnetic field has a value of about seventy-six gausses, with the axis of suspension in the principal plane. The sphere should normally point, of course, with the plane of symmetry parallel to the magnetic field, because this is the direction of maximum susceptibility. However, if the sphere has been exposed previously to a stronger field, the residual magnetization along the axis might be sufficient to deflect the sphere so that the positions of equilibrium would make an obtuse angle with one another, and this is just what I observed on suspending the sphere. No rotation in the weaker field sufficed to prevent this deviation, though the application of a stronger field changed the sign of the deviation.

Further, the hysteresis in the principal plane was shown by the fact that the sphere might be rotated some 110° to 120° from the position of equilibrium and still return through the obtuse angle, and the fact that, when hung with the axis of the crystal vertical, the sphere when rotated would drop back some 20° to 30°, though if this were allowed for, it might be made to point in any desired direction.

For the two principal directions in the crystal, that is, along and perpendicular to the axis, I have obtained the magnetization curves which are shown in Fig. 3. The points up to field strengths of about 1,500 were obtained with sphere 9. The values at higher fields are for sphere A_4, for sphere 9 was too large to be introduced into the narrower jaws of the pole pieces (No. 1) used at these higher fields. My only dependable value for the direction of the minimum in A_4 is indicated by a cross (+). I have not as yet obtained values for I for crystals of this type below the field strengths here shown, for the strong hysteresis complicates the problem of these determinations.

For intermediate positions readings which exhibit the symmetry of the crystals are plotted in Fig. 8, which shows the component of the intensity parallel to the field for different field strengths in terms of fractional parts of the maximum intensity. The open and the dashed circles represent opposite halves of the zone and the two are so superposed as if the points were plotted for the whole 360 degrees on transparent paper and the plot were then folded over at the maximum. The curves 1, 2, and 3 are for sphere 9, in which the axis is indicated by 90° and the principal plane by 0° and 180°. The axis is very nearly in the zone of the plot, as is shown by the curve 3*a*, which is obtained by rotating the magnet through small angles in a horizontal circle, when the specimen is set for the minimum of the zone plotted in the curves. Curve 5 is for

a zone that is nearly, but not quite, perpendicular to the axis, and indicates that the sphere is isotropic in this plane, within the accuracy of the measurements here plotted. The curve marked 4 is for spheres (A_2 and A_4), which exhibit properties similar to sphere 9, at a field strength a little higher than the others. The values for A_4, large circles in curve 4, are for a zone that does not quite contain the axis.

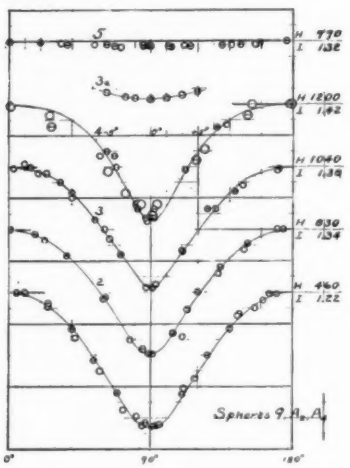


Fig. 8.

Tests on Elba Hematite Spheres (Ferromagnetic). Curves 1, 2, 3, sphere 9, axial zone. Curve 4, spheres A_2 and A_4, nearly axial zones. Curve 5, sphere 9, zone nearly perpendicular to the axis. Curve 3*a*, sphere 9, zone perpendicular to 1, 2, and 3, to a magnified scale showing test for minimum. The ordinates give the intensity of magnetization, in terms of the maximum for the zone, which is taken as one. The curves are displaced vertically to avoid confusion.

Curves 1, 2, and 3, in which the fringe shifts for the direction of maximum intensity are respectively 5.25 fringes, 11.75 fringes, and 15.6 fringes exhibit not only a successive increase in the relative value of the minimum intensity, but also a gradual slight change in the character of the curve. The maximum is less sharp for the higher field strengths.

Each of the points on these curves represent the mean of at least two readings with the field in opposite directions, and between readings the specimen was demagnetized by reversals in order to eliminate as much as possible the effect of hysteresis. This was difficult to accomplish at times, both for the direction of the minimum and for oblique directions fairly close to that, the hysteresis being so troublesome in the direction of the minimum that at times it seemed almost impossible to eliminate its influence and get concordant readings. In practically every case persistence and care in demagnetizing by reversals finally did demagnetize the specimen, until the same readings could be obtained by reversing the field.

SUMMARY.

The results of this investigation upon the magnetic properties of hematite may be briefly stated as follows:

1. The symmetry of hematite is magnetically that of an axis of symmetry, with a plane perpendicular thereto in which the magnetic susceptibility is independent of the orientation.[1]

2. In this principal plane hematite is ferromagnetic and exhibits

[1] Consult, however, Kunz, loc. cit., pp. 73, 82.

hysteresis. The magnetic intensity is low and does not approach saturation for fields as high as 4,000 gausses.

3. Parallel to the axis the specimens from many different localities are paramagnetic, but some specimens from Elba exhibit strong hysteresis, as Westman also found, working at low fields with Kragero hematite.[1] In all cases within the range of field strength available, the intensity of magnetization along the axis is much less than in the principal plane.

4. For intermediate directions, the direction of magnetization does not coincide with the field, and in certain positions the couple exerted upon the material is relatively large. The component parallel to the field has maxima and minima at angles of ninety degrees, as Weiss found for magnetic pyrites.[2] I have not yet measured the component perpendicular to the field.

It should be noted that the values for the intensity of magnetization here found are in all cases less than those found by Westman and by Kunz. Westman, using a magnetometer method and small rods of hematite, has obtained hysteresis loops with a maximum field strength of about seventy gausses. The ascending and descending limbs of these curves are almost identical above thirty gausses, and for this range his values are about twice what one would expect from an extrapolation of the magnetization curve for the principal plane of sphere 9. Except for the lack of agreement in the values of the intensity, the specimens of Westman are apparently of much the same nature as is sphere 9 above, in that they show hysteresis in an increasing amount as the direction of the field gets closer to the magnetic axis of the crystal. The accuracy of his work did not permit the plotting of hysteresis loops for the direction of the axis.

Kunz,[3] who made use of over 100 different individual crystals from different localities, says that the induced current, which was set up in a stationary surrounding coil when a crystal was jerked out of a magnetic field, indicated that every specimen he tried was paramagnetic for field strengths as high as 600 gausses. However, the constants he gives vary widely, in the ratio of fifty to one, and it is evident from the work above that such variations would not be called forth by any lack of accuracy in setting the specimen. The smallest of his constants is almost twice the value obtained in the work above for sphere *G*, and the observed susceptibility, taking the smaller values, very nearly agrees with the value for sphere 9 at 600 gausses, though this latter shows strong hysteresis at higher fields.

[1] Loc. cit.

[2] Weiss, Journal de physique, 4: 469, 1905.

[3] Loc. cit.

A REDETERMINATION OF THE ABSOLUTE VALUE OF THE COEFFICIENT OF VISCOSITY OF AIR.

BY ERTLE LESLIE HARRINGTON.

IN view of certain results on the "Coefficients of Slip" obtained by him from his study of the laws of fall of small spheres in gases, Prof. Millikan suggested to me that I attempt to check these results by making some measurements on the coefficients of viscosity at very low pressures with the constant deflection apparatus designed by himself and Dr. Gilchrist. In the course of this work the method was so perfected as to make it capable of a precision apparently unapproached heretofore in measurements on the viscosity of gases.

Since the knowledge of the exact value of this coefficient for air is of such fundamental importance in many lines of physical research it seemed worth while to turn aside for the sake of attempting again to fix its value with all the precision possible. This was especially needed since some question[1] has been raised recently relative to the reliability of the estimate made by Prof. Millikan as to the most probable value of this constant. From determinations made under his direction by Gilchrist[2] by the constant deflection method, and by Rapp[3] by an improved capillary tube method, taken in connection with reliable determinations made elsewhere and by other methods, Prof. Millikan published[4] as the most probable value of this constant, η, at 23° C., .0001824, and estimated its uncertainty at not more than one tenth per cent.

In connection with another problem, Vogel,[5] in 1914, was led to make and publish a summary of the results of nearly all the determinations of this constant that had ever been made, but he arrived at a value about .8 per cent. higher than the above. In this, however, he includes determinations which certainly involve gross error and which are at least very far from what is now known to be the approximate value of η. In fact, he lists values with a total range of nearly 11 per cent., even in the same method, while observers with present laboratory methods and facilities,

[1] A. Gille, Ann. der Phys., 48, p. 799, 1915.
[2] PHYS. REV., I., p. 124, 1913.
[3] PHYS. REV., 2, p. 363, 1913.
[4] Ann. der Phys., 41, p. 759, 1913.
[5] Ann. der Phys., 43, p. 1235, 1914.

using any method whatsoever, would admit no greater error than a fraction of a per cent., hence the inclusion of such widely variant values of η renders more doubtful the validity of any mean so obtained.

The determination by Gilchrist appears also in this summary by Vogel, and although he gives it relatively more weight than any other single determination by any method, he nevertheless expresses the feeling that the method and theory had not as yet received full development. Since the publication of the Gilchrist article the method has been used by Timiriazeff,[1] but his experimental arrangements were such as to make it better suited to relative than to absolute determinations. It therefore seemed important to subject the method itself to as critical a study as possible while making the new determination of η.

APPARATUS.

The apparatus is the same as that used by Gilchrist save for the suspension and for certain other features which it was necessary to modify in order to adapt it to running in vacuum. The diagram shows the general arrangement of the apparatus. The outer, *O*, of two concentric brass cylinders is made to rotate with constant velocity about the inner, *I*, which is suitably hung by an elastic suspension. The viscosity of the air produces a drag upon the inner cylinder causing it to be deflected from its position of rest to such an angle that the restoring couple of the suspension brought into play exactly counteracts the drag of the air, the angle of deflection being measured by the usual mirror telescope and scale method.

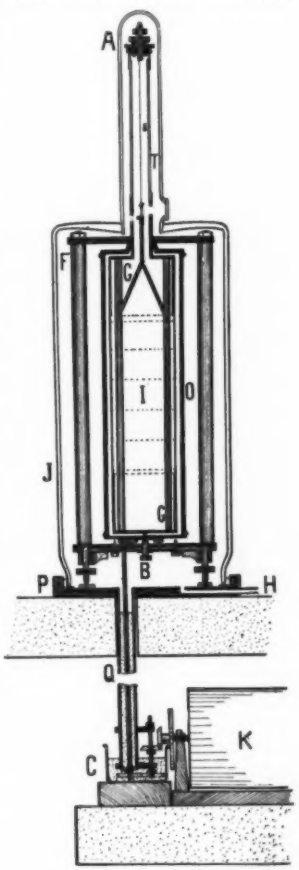


Fig. 1.

The cylinder frame, *F*, is mounted upon a heavy steel plate, *P*, accurately machined and having a raised rim in order to provide a mercury seal for the large glass jar, *J*, which covers the whole. To one side of the plate is drilled a hole to provide pump connections, and in the bottom is screwed a steel pipe, *Q*, enclosing the driving shaft, and of such length as to serve as a barometer column, and the lower ends of pipe, rod, and gearing were suitably constructed to dip into a mercury cup,

[1] Ann. der Phys., 40, p. 971, 1913.

C, through which the motion must be transmitted. The cylinders are carried by a heavy brass frame, *F*, provided with leveling screws and levels. The outer cylinder is supported on a slightly conical bearing, *B*, at the bottom, and at the top rotates on the tube, *T*, as an axle. The tube, *T*, at the same time supports the suspension head, *A*, and is rigidly held by the main frame. To eliminate end effects the inner cylinder is provided at either end with a guard cylinder, *G*, of the same radius, and rigidly held at a small distance from it and in perfect alignment with it by three brass posts which connect the two guard cylinders and suitable end disks. The upper part of this guard system and the suspension tube above mentioned are constructed as one piece so that the upper guard cylinder is held accurately centered with respect to the upper part of the rotating cylinder. The lower part rests on a conical bearing which is a part of, and accurately centered with respect to the bottom of the outer cylinder. The suspension head, *A*, is so constructed as to permit considerable translatory motion in any direction, as well as rotatory, thus making possible accurate adjustment. The above apparatus was constructed with great care and precision by Wm. Gaertner & Co., and to them much credit is therefore due for the success of the experiment. Such accuracy in construction made it possible to have the guard cylinders very close (.025 cm.) to the suspended cylinder, and thereby completely eliminate the need of end effect corrections.

A chronograph, *K*, provided with extra weights serves the double purpose of driving the apparatus, and also of leaving a permanent record of the speed of rotation. It was so arranged that the cylinder could be instantly thrown out of gear and the chronograph used independently of the other apparatus, this being done each time the period of vibration of the inner cylinder was determined.

A Beckmann thermometer, calibrated with a standard Baudin thermometer, and reading directly to .01 degree was hung beside the outer cylinder. A high-grade Centigrade thermometer graduated to .1 degree was hung beside it to serve as a check. The room itself was one of the constant temperature rooms of the Ryerson laboratory; a basement room, with no windows, lined on all sides, top and bottom, with a 5-in. layer of cork, and provided with heavy inner and outer doors. The room was efficiently heated by a new style electric heater (furnished by the Lee Electric Radiator Co.) used in connection with a sensitive thermostatic control, and the air was constantly stirred by a large fan. The temperature control was such that during any run the temperature variation recorded by the Beckmann thermometer was never more than a few hundredths of a degree, and often no change at all was detected.

The air in the apparatus was kept dry by an enclosed dish of phosphorus pentoxide.

CRITICAL STUDY OF APPARATUS AND DETERMINATION OF DIMENSIONS.

Inasmuch as one of the objects of the experiment was to study the possibilities of the method as well as to find the absolute value of η, considerable time was spent on this phase of the work, and whenever

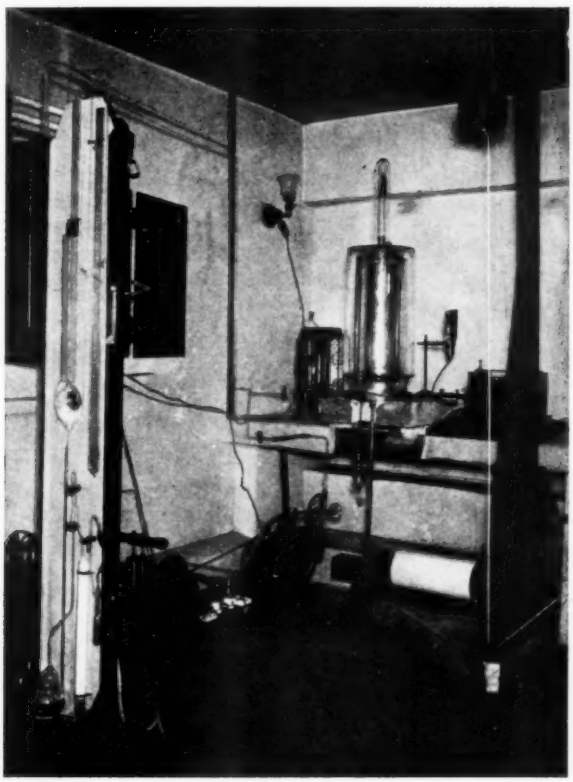


Fig. 2.

possible various methods of measurement were used for the purpose of cross checking.

1. *The Inner Cylinder.*—Three methods were used to measure the diameter of the inner cylinder. In order to insure getting different diameters and to entitle each different one to equal weight in the computation of the mean a large number of points evenly distributed over the surface of the cylinder were systematically numbered and the measurements were taken at these points. The first method was to place the cylinder vertically on the bed of a dividing engine having mounted at one

side with its axes perpendicular to the direction of motion a short focus telescope provided with cross hairs. The distance between tangent lines was then determined from the screw readings. The second method was to adjust the jaws of a large-size vernier caliper to the diameter of the cylinder and then determine the perpendicular distance between the locked jaws by placing the same on the bed of the dividing engine, and measuring by the usual method. The third method was to use a micrometer screw caliper of sufficiently large size to measure directly the diameter. The last two methods were by far the more convenient and yielded as accurate results. These two results differed by only 1 part in 13,000, and their mean agreed to Gilchrist's value to within 1 part in 6,000, which is a liberal estimate of the possible error in this dimension. The length was determined by cathetometer methods, and the value found to agree exactly with that given by Gilchrist, and is probably correct to within 1 part in 6,000.

2. *The Outer Cylinder.*—The most satisfactory method of measuring the diameter of the outer cylinder was found to be by filling it with distilled water observing the temperature and depth, and weighing the water used. Results thus obtained differed by only 1 part in 15,000, and the mean differed from that by Gilchrist by exactly the same amount, so the error is perhaps no more than 1 part in 8,000.

The accuracy in the inner surface was studied in this way: The inner cylinder, the lower guard ring, and the posts were removed, leaving the upper part of the guard cylinder system, which, as above described, form the axle for the outer cylinder. A heavy rod with one end hollowed out to fit the conical bearing in the bottom of the outer cylinder was inserted in the opening and brought to rest on the bearing. This rod carried a lever arm suitably curved to rest against the wall of the cylinder, capable of being adjusted to different heights, and bearing at the fulcrum a mirror. A suitable telescope with vertical scale placed at a distance of nearly three meters made it possible to detect the slightest deviation from constancy in the radius or perfection in symmetry. In doing this the lever was held lightly against the wall by a weight, and the cylinder slowly rotated at a constant speed. From the readings of the observer at the telescope and a measurement of all distances concerned, any variations could be quantitatively determined. It is important to note that this method not only tests the accuracy of the inner surface but tests also the symmetry of this surface about the same bearing that is to carry and hold in position the inner cylinder system. The results of this test were very satisfactory, inasmuch as the variations were of the order of 1 part in 2,500 and of such nature as to be self-counteracting in their

effect on the final results, which were therefore affected probably less than 1 part in 5,000.

3. *Moment of Inertia of the Inner Cylinder.*—This was found as usual by determining the period of vibration of the cylinder alone, and then when a known moment of inertia was added. The cylinder was suspended by piano wire and the cylindrical surface made plumb and symmetrical about the axis by suitable adjustment of the three support bars which connect the cylinder with the suspension clamp, and by use of small weights fastened to the upper supporting vane of the cylinder. The heavy, double support of the clamp from which the cylinder was suspended rested on a stone bench, and although the room was apparently free from air currents the cylinder was surrounded by a much larger one in order to insure entire absence of them. The passage through the zero position of the cylinder was indicated by the flash of a light into a telescope at the opposite side of the room, and an electric key enabled the operator to accurately register this time on the chronograph. The time divisions were marked by impulses from the standard laboratory clock and involved no appreciable error whatever, and the divisions could be read to one one hundredth of a second. By taking the period from a rather long run thus measured, the individual runs varied from the mean for any suspension by an amount of the order of 1 part in 10,000, which may be considered the probable error from this source. The added known inertia consisted of a bar and ring, accurately machined, and placed on the cylinder symmetrically. The dimensions of the ring and bar were determined on the dividing engine, and their weights by the analytical balance. The inertia of the combined ring and bar was computed by the usual formula derived for such bodies, and the result agreed to 1 part in 8,000 with that obtained by Gilchrist, this ratio probably representing the accuracy of this determination. No faulty adjustment to symmetry about the axis of suspension could have been constant to the different series of runs, since the ring and bar were frequently removed and replaced.

Having the two periods and the one known inertia, the moment of inertia of the inner cylinder was computed from the usual formula,

$$\frac{T_1^2}{T^2} = \frac{I + I_1}{I}.$$

The average departure of the various results from the mean for the moment of inertia of the inner cylinder obtained from the different suspensions used was 1 part in 5,000 and the mean differed from that obtained by Gilchrist by exactly the same amount.

DIMENSIONS.

Dimensions that are not involved in the computation of the results are here included for descriptive purposes, but only approximate values for such are given.

Vertical distance from base of chronograph to extreme top of cover	185 cm.
Diameter and height of glass jar, respectively	28 and 62 cm.
Length of outer cylinder	46
Length of suspension	23.5
Length of each guard cylinder	10
Length of inner cylinder	24.88
Distance between guard cylinders	24.93
Weight of inner cylinder	321 g.
Radius of outer cylinder	6.06317 cm.
Radius of inner cylinder	5.34116
Moment of inertia of inner cylinder (experimentally determined)	7,617.3

ADJUSTMENT OF INSTRUMENT.

Before being placed in the instrument the inner cylinder was again tested for symmetry and perpendicularity with the same methods and precautions used preliminary to the determination of its moment of inertia. In this three plumb bobs instead of one were used for the purpose of expediting matters and permitting simultaneous observations in three directions without in any way disturbing the cylinder or plumb bobs.

The lower end of the outer cylinder being in place, the inner cylinder and the guard cylinder system were put into position, fastened rigidly by the top brace, and after suspending the inner cylinder the suspension head screws and the leveling screws of the base of the instrument were so manipulated as to bring the surface of the guard cylinders into alignment with the inner cylinder as perfectly as possible without the use of a telescope. The outer cylinder was then put into position, the suspension tube again clamped, and the deflection of the inner cylinder noted as the outer cylinder was rotated at the speed to be used later in determinations. The suspension head was then rotated until the zero position was brought as much to one side as the deflection position was to the other side of the telescope which was in the middle of, and perpendicular to the scale. Three small support screws in the base of the instrument were then brought just to touch the bottom of the outer cylinder in order to hold it in its exact position during the final adjustment. The outer cylinder was loosened from its bottom and removed and the top brace replaced and fastened firmly in position. The final, and more careful adjustment of the guard cylinder system to alignment with the inner cylinder was made by means of a short focus telescope. With a suitable

clamp system attached to the frame the outer cylinder was replaced without at any stage of the process inclining or otherwise disturbing the inner cylinder. The preliminary adjustment to zero position made unnecessary the turning of either the guard cylinder system or the suspension head after this final adjustment, and thereby eliminated any error that might have come from a lack of perfect coincidence of the suspension with the axis of the suspension head collar. The use of the support screws for the base of the outer cylinder holds it, and therefore the lower end of the inner cylinder system, in precisely the position they occupy during a run. Keeping the guard cylinder system in place while replacing the outer cylinder eliminates the question as to whether it returns to the exact position it had during adjustment. With these precautions it would seem unlikely that any appreciable error could arise from faulty adjustment, and the results later given involving results obtained before and after dissembling and readjusting furnish convincing evidence of the absence of such error.

TRIAL RUNS AND A STUDY OF FACTORS AFFECTING RESULTS.

As will appear later, the value of η is computed from the time of rotation, the period of vibration of the inner cylinder, the deflection, the distance to the scale, and the temperature observations. The method of taking these observations was this: The zero position was read when the cylinder was at rest and checked by causing the cylinder to make small vibrations (about 1 cm. as seen on the scale) and determining the zero position as is done in using balances. This was done as a precaution against any error due to sticking, although experience showed this step really unnecessary. The outer cylinder was then put into rotation, the speed at first being modified by a brake attachment to the chronograph which could be operated from the position of the telescope in order to bring the inner cylinder quickly to near rest in its deflected position. As soon as a steady state was attained the stylus was lowered on to the waxed paper of the chronograph drum and the rotation continued until the stylus had traveled the length of the drum, which meant, with the speed used, an interval of about 13 min. In practice the inner cylinder was allowed to vibrate through two or three millimeters as seen on the scale, readings being taken at short intervals; this plan giving a large number of independent readings, eliminating the barely possible source of error due to sticking, and affecting a great saving of time that would otherwise be required to bring the cylinder to absolute rest, inasmuch as the period of vibration was very long, and the damping very small. At frequent intervals during this period the temperature was read on

the Beckmann thermometer. At the close of the run the cylinder was slowly let back and its zero position again checked. Now the outer cylinder was given a rotation sufficient to set the inner cylinder in vibration, and then thrown out of gear, thus allowing the chronograph to be used merely as such, whereupon the period of vibration was taken over a period of about 45 min. To do this an electric key at the position of the telescope enabled the operator to make accurate chronograph record of the passage through the zero position, the first five and the last five being recorded in order to provide means of cross checking and thus insure absence of appreciable error from this source. The periods thus obtained were probably accurate to within 1 part in 8,000.

The scale on which the deflections were read was a carefully selected straight meter stick tested with a standard metric steel scale. The magnification of the telescope was such that .1 mm. could be read easily and since the deflections were of the order of 600 mm. the readings were probably correct to within 1 part in 6,000. A steel tape was used to set the ends of the scale equidistant from the mirror and to determine its perpendicular distance from the mirror. The error in this was probably not greater than 1 part in 6,000.

Irregularities in the speed of the chronograph might offer a source of error, not on account of uncertainty as to what the speed is, for that is obtainable directly from the record, but on account of the resulting unsteadiness of the deflection. Fortunately it was found that the chronograph drove the apparatus at a very constant speed, though of course not perfectly so, owing perhaps to the irregularities in the friction, or a lack of perfection in the gearing. However, a small auxiliary weight, at the side of the operator, brought into series with the main weight by two pulleys, enabled him after some experience to almost completely neutralize any such irregularities, thereby reducing the error from this source to probably 1 part in 5,000.

The high consistency in the early trials in the results for any suspension indicated a satisfactory control in all the above sources of error, but it was found that variations in the suspension produced rather great variations in the results. In view of the experience of Gilchrist the bifilar form of suspension was tried at first, but on account of the rather great weight (321 g.) of the inner cylinder, and its small distance (.25 mm.) from the guard cylinders which permitted no sag, it was not possible to use silk fibers which permit, perhaps, the closest approach to the true bifilar type. Metallic ribbons were therefore used, but after two months of experience with them they were wholly discarded, since it was not found possible to entirely eliminate the effect of a change in the ribbon

or even of a mere change in the separation of the strands or in the manner of clamping, upon the results obtained. The trouble no doubt lies partially in the rather great discrepancy between such a bifilar and those ordinarily treated theoretically since the deflection brings into play not only a restoring couple due to the slight raise in the weight, but also a restoring couple due to the twist in the strands themselves. Such a suspension is therefore a sort of hybrid between the bifilar and the ordinary elastic unifilar suspension. The greatest error, however, probably comes from the fact that the ribbons have widths of the same order of magnitude as the separation of the strands which makes it quite likely that as deflection occurs the two edges of either strand may assume varying portions of the load, thereby causing a virtual change in the distance between the strands. If the strands be clamped at both ends it is unlikely that the load is equalized between the two strands, and if instead the strand be simply looped about a pin at one end in order to permit constant equalization of the load there is the possibility of error due to a rolling of the strands about the pin as the deflection occurs. Unrolled phosphor bronze wire in place of the ribbon was even less satisfactory owing to the residual coil and the consequent drift, nor was either found satisfactory later as a unifilar suspension. In fact the writer was led to conclude that little dependence could be placed on phosphor bronze where precise results are expected. Quartz fibers were tried, but it was not found possible to obtain fibers coarse enough to support the rather great weight and at the same time fine enough to give sufficient deflections. The smallest piano steel wire obtainable was much too stiff, but it was found possible by reducing the size of the smallest obtained, by very carefully rubbing with fine emery paper, to secure a sufficiently large deflection and yet retain adequate tensile strength. After the adoption of this plan no further suspension troubles were experienced. A number of such were made, and in all cases there was a good zero return and a satisfactory absence of drift. Moreover, different suspensions, though differing greatly in stiffness, yielded entirely concordant results. Later some samples of the uncoiled stock from which the hair springs of watches are made were furnished by the Elgin Watch Company and found to have the proper range of stiffness.

As will be seen later the torsion constant of the suspension is expressed in terms of the inertia of the inner cylinder and the period of vibration. From the observed damping, and the theoretical relation between the magnitude of damping and the effect on the period as given, for example, by Helmholtz, it was calculated that the total effect due to the damping factors would be of the order of 1 part in 10,000, or quite inappreciable.

Moreover, by experiment no effect on the period could be observed when the outer cylinder was removed and the guard cylinders were separated many times as far from the vibrating cylinder. But, although such factors as viscosity involved above do not appreciably affect the period, the fact must not be overlooked that the vibrating cylinder does carry the air with it, and the moment of inertia of this air must be taken into account. This point was first called to my attention by Dr. Lunn. The periods taken in vacua were actually found to be 1 part in 750 less than the periods taken at ordinary pressures, so the data given make due allowance for this effect.

COMPUTATION OF RESULTS.

For the calculation of the results the well-known and very simple formula[1] was used in this form:

$$\eta = \frac{\pi\phi I(b^2 - a^2)}{a^2b^2T^2\omega l},$$

where η is the coefficient of viscosity, I the moment of inertia of the inner cylinder, a and b the radii of the inner and outer cylinders respectively, l the length of the inner cylinder, ϕ the angular deflection of the inner cylinder, T the period of vibration of the inner cylinder, and ω the constant angular velocity of the outer cylinder. If the period of rotation of the outer cylinder, t, be substituted for $2\pi/\omega$, and a constant, K, for the product $[I(b^2 - a^2)]/(2a^2b^2l)$ (having here a numerical value of 1.20188) the formula becomes:

$$\eta = \frac{tK\phi}{T^2} \quad \text{or} \quad \eta = \frac{tK}{T^2}\tan^{-1}\frac{s}{2d},$$

where s is the deflection as read on a straight scale, and d the distance of the scale from the mirror. The latter form was used in all computation. A development of the above formula involving a more general treatment which considers the coefficient of slip will be given in a paper, following this, which will consider the problem of viscosity at the low pressures where the effect of slip becomes appreciable. In apparatus of the dimensions here used the correction for slip at ordinary pressures amounts to about 2 parts in 100,000.

All determinations were made at temperatures in the neighborhood of 23° C., and the values for η reduced to that temperature by the use of the formula suggested by Prof. Millikan (l. c.),

$$\eta_{23} = \eta_\theta + .000000493(23 - \theta),$$

where η_θ is the value of the viscosity coefficient obtained at θ° C. This

[1] See Poynting and Thompson, Properties of Matter, p. 213.

simple formula, found satisfactory through the range mentioned by him must certainly hold in the small ranges here involved, which are, with but two exceptions, less than one degree.

RESULTS.

The following data show the results of thirty-one determinations of η made at various times during about three months, and involve the use of six different suspensions. Suspensions *C* and *D* were really the same suspension under different physical conditions. In most cases during the series of runs for a given suspension the apparatus was taken apart and readjusted in order to make sure there was no error of adjustment.

Sus.	d (Cm.).	s.	θ.	t.	T.	$\eta_{23} \times 10^7$.
A	200.0	40.21	23.97	30.059	140.70	1,823.7
A	200.0	40.26	24.45	30.020	140.61	1,823.5
A	200.0	40.06	23.06	30.018	140.62	1,820.9
A	200.0	40.05	23.31	30.085	140.62	1,823.3
A	199.7	40.025	23.18	30.000	140.58	1,821.4
B	200.2	35.81	23.61	30.014	132.81	1,821.2
B	200.2	35.665	22.88	30.114	132.79	1,824.1
B	200.2	35.73	23.14	30.031	132.79	1,821.0
B	200.2	35.837	23.43	29.971	132.80	1,821.2
B	200.2	35.80	23.46	30.032	132.80	1,822.8
C	200.8	60.51	22.88	30.090	172.13	1,825.9
C	200.8	60.67	23.055	29.940	172.14	1,820.5
C	200.8	61.064	22.93	29.840	172.21	1,825.1
C	200.8	60.624	23.165	30.014	172.18	1,822.2
C	200.8	60.604	22.84	29.962	172.13	1,821.1
C	200.8	60.68	23.09	29.936	172.13	1,820.8
C	200.8	60.73	22.91	29.940	172.13	1,823.1
C	200.8	60.77	23.19	29.907	172.14	1,821.0
C	200.8	60.75	22.90	29.895	172.14	1,820.9
C	200.6	60.905	24.10	29.912	172.13	1,822.7
C	200.6	60.54	23.00	29.982	172.10	1,822.0
D	200.7	61.154	22.97	30.014	172.98	1,822.9
D	200.7	61.216	22.99	29.954	172.95	1,821.6
D	200.7	61.07	23.22	30.075	172.96	1,823.2
E	200.85	51.66	23.27	30.178	159.39	1,824.8
E	200.85	51.168	23.28	29.888	159.39	1,824.7
F	200.9	63.34	23.16	29.946	175.62	1,823.8
F	200.9	62.988	23.26	30.087	175.60	1,822.3
F	200.9	62.957	23.11	30.103	175.56	1,824.0
F	200.9	62.974	23.10	30.066	175.58	1,821.9
F	200.9	63.093	23.19	30.008	175.55	1,821.9

Mean value of η at 23° C. $= 1822.6 \times 10^{-7}$.

Moreover, the runs show such variations in the various factors involved as to make each determination an independent one, and no determination made with satisfactory control in the manipulation of all steps was discarded.

The strongest evidence of the advantages of this method for the determination of η lies in the remarkable consistency of the results here shown. If from the individual deviations from the above mean one computes the probable error by the usual least square method the result is found to be .19 or 1 part in 9,600. Moreover, it should be emphasized that this really *includes every* source of error except those involved in the instrument constant, K. The probable error for each of the various determinations involved in this constant has been given above in detail and if the probable error in this constant be computed by the same method as above it is found to be 1.9 parts in 5,000. The combined or total error would be by this method of calculation only 1 part in 2,500 or .04 per cent. Moreover, if the means for the different suspensions be compared it is found that the maximum variation from the above mean is less than .03 per cent. with the one exception of suspension E, a watch-spring suspension the use of which was discontinued on account of its tendency to drift. Considering these two striking results, and making any reasonable allowance for any unreliability in the least square method of computing errors or of the estimates made of any individual probable error it seems entirely justifiable to claim that the above mean is correct to within less than .1 per cent. of the true value of η at the temperature considered.

A comparison of the consistency of these results with the lack of consistency of the results obtained by any other method, more especially by the capillary tube method, shows the marked superiority of this method. The uncertainties of the capillary tube method need not be considered here inasmuch as they are well known and have been discussed by Prof. Millikan,[1] by Fisher,[2] Vogel,[3] and others. Only a few points of contrast need be mentioned; the capillary tube method is based on incomplete theory since it does not consider the effect of the radial component of the velocity and other uncertainties due to the increase in the volume of the gas as it passes along the tube, the general end effects in addition to the question of the effect of irregularities in the bore upon the stream lines, the difficulties in getting the exact pressures, and above all, the impossibility of getting perfect tubes of the small radii usually employed, and the great difficulty of subjecting any tube selected to accurate examination as to uniformity, circularity, and even as to

[1] L. c. [2] PHYS. REV., 29, p. 147, 1909. [3] L. c.

the value of the radius itself, which enters, it should be recalled, in the fourth power. The wide variation in the results obtained by this method by different observers, and even by the same observer with different tubes, is ample proof that these uncertainties exist. On the other hand, with the method described above the theory is complete, there are no end corrections involved, no expansion takes place, every step in the construction of the cylinders is subject to control, the dimensions are so great that they may be determined with great accuracy, and every portion of the apparatus is subject to minute study for irregularities, and even should such exist, their effect would be far less serious than in the case of the other method. As to consistency with other observers we are essentially limited to the value obtained by Gilchrist who first used the method and made the claim that his result contained not more than .2 per cent. error. The value here obtained differs from his by less than that amount. That his values fluctuate through a greater range than the range here obtained is without doubt due principally to the suspension troubles mentioned above which were here so largely eliminated, for every determination of his of any instrument constant that could at this time be checked was most critically examined, and no one of them found to differ by more than 1 part in 6,000 from the value here given.

It is interesting to note that Rapp,[1] who perhaps came more nearly completely eliminating the errors in the capillary tube method than anyone else, and who used a large number of tubes, is practically identical with the result here obtained, as is also that obtained by Hogg,[2] who used an oscillation method. The result obtained by Grindley and Gibson,[3] using still a different plan differs only by about .03 per cent. More significant still is the fact that the value published by Prof. Millikan as correct to within .1 per cent. is less than .08 per cent. above the value here obtained, and as his value was based on perhaps the most accurate determinations by five different methods, it would seem that the above claim that the result here obtained is within .1 per cent. of the true value is well founded, since the above mentioned values all lie well within this limit.

In conclusion the writer wishes to acknowledge his gratitude to Prof. Millikan, who suggested the problem and maintained such constant and helpful interest in the research during its progress, and to Prof. Michelson, the head of the department, for various helpful suggestions.

RYERSON PHYSICAL LABORATORY,
UNIVERSITY OF CHICAGO,
June, 1916.

[1] L. c.

[2] Am. Acad. Proc., 40, 18, p. 611, 1905.

[3] Proc. Roy. Soc., A, 80, p. 114, 1908.

NEW BOOKS.

The Science of Musical Sounds. By DAYTON CLARENCE MILLER. New York, The Macmillan Company, 1916. Pp. viii + 286.

This volume presents the substance of a course of Lowell Institute lectures delivered in 1914 before audiences who had certainly a great privilege in hearing a subject of universal interest expounded in so delightful a manner by the most competent expert in it.

A popular course of scientific lectures, designed for a general and non-technical public, may well be somewhat sketchy and incomplete; but the volume before us shows, once more, that this is by no means inevitable. In reality, we have a number of instances of such lecture courses, published later in book form, which while thoroughly popular in the best sense excite only admiration in the hearer or reader who is well trained in scientific matters and already somewhat familiar with the particular subject in hand. Upon thinking over the list of such books and the great names of the men who have produced them, we may well be proud that a member of the American Physical Society has made a notable addition to the list.

One of the striking facts about the book, and one which speaks for itself, is that while a large part of it relates to Professor Miller's own investigations, the whole is not thereby thrown at all out of balance. And this happy result is not due merely to artistic presentation but to the interest and importance of the author's work.

A detailed review seems quite unnecessary, and any further recommendation whether to the professional physicist or to the general reader interested in music, would be superfluous.

E. B.

ERRATA

Vol. VII., June, 1916, article by Arthur H. Compton, entitled "A Recording X-Ray Spectrometer, and the High Frequency Spectrum of Tungsten"; on page 654, the third column of Table I., the wave-length of the tungsten lines, should be changed as follows:

Line.	θ	Instead of $\lambda \times 10^8$ Cm.	Should Read $\lambda \times 10^8$ Cm.
a	9° 44.5′	1.0387	1.0249
b	9° 53.1′	1.0539	1.0399
c'	10° 3.7′	1.0725	1.0582
c''	10° 7.7′	1.0796	1.0652
d	10° 25.7′	1.1107	1.0959
e	11° 36.3′	1.2349	1.2185
f	11° 49.9′	1.2587	1.2420
g	12° 0.4′	1.2771	1.2601
h	12° 11.4′	1.2962	1.2787
i	12° 22.7′	1.3160	1.2985
j	12° 44.7′	1.3543	1.3363
k	14° 4.7′	1.4933	1.4735
l	14° 11.1′	1.5044	1.4844

Vol. VIII., August, 1916, page 97, article by R. C. Tolman and T. D. Stewart, entitled "The Electromotive Force Produced by the Acceleration of Metals"; page plate containing Fig. 2 and Fig. 3 to face page 104, will be found in September number.

Vol. VIII., August, 1916, article by F. Schwers, entitled "Compton's Formula for the Temperature Variation of the Specific Heat of Solids"; in Table IX., page 124, the sixth number of the fourth column should read 0.0923 instead of 0.0756.

Index to Volume VIII., Series II.

A.

Absorption Spectrum, The Effect of Temperature upon the, of a Synthetic Ruby, *K. S. Gibson*, 38.

Absorption, The Law of, of X-Rays at High Frequencies, *Albert W. Hull* and *Marion Rice*, 326.

Absorption Coefficients, The, of Soft X-Rays, *C. D. Miller*, 329.

Absorption, The Fluorescence and, of Certain Pleochroic Crystals of the Uranyl Salts, *Edward L. Nichols* and *H. L. Howes*, 364.

Adsorption, The Evaporation, Condensation and Reflection of Molecules and the Mechanism of, *Irving Langmuir*, 149.

Alpha Rays, On the Ionization of Gases by, *H. A. Bumstead*, 715.

Amalgams, Change of Resistance with Temperature of Various Sodium, *Ralph C. Rodgers*, 259.

B.

Bumstead, H. A., On the Ionization of Gases by Alpha Rays, 715.

Becknell, Guy C., On the Demagnetization of Iron and Steel Rods by Strain and Impact, 504.

Benade, J. M., The Nature of the Collisions of Electrons with Gas Molecules, 449.

Beta Rays, The Magnetic Spectra of the, of Radium De and of Radium and its Products, Determined by the Statistical Method, *Alois F. Kovarik* and *L. W. McKeehan*, 574.

Bidwell, C. C., Resistance and Thermoelectric Relations in Iron Oxide, 12.

Black Body, The, at the Melting Point of Platinum as a Fixed Point in Photometry, *Herbert E. Ives*, 250.

Black Body, Note on, Brightness Equation Based on Equivalent Wave-Lengths, 323.

Bohr's Theory, The Dispersion of Hydrogen and Helium on, *C. Davisson*, 20.

Borelius, G., On the Electrostatic Measurements of Electrode Potentials, 128.

Bridgman, P. W., Tolman's Principle of Similitude, 423.

Brown, F. C., The Frequent Bursting of Hot Water Pipes in Household Plumbing Systems, 500.

Buchner, G. J., Note on the Parson Electrometer, 248.

C.

Canal Rays, The Properties of Slow, *A. J. Dempster*, 651.

Capillary Tube Method, The Coefficient of Viscosity of Air by the, *Effie Markwell*, 479.

Cathode Fall, The Theory of the, of Potential, *H. A. Wilson*, 227.

Cathode Rays, An Experimental Verification of the Law of Variation of Mass with Velocity for, *Lloyd T. Jones*, 52.

Carbino Effect, The, in Various Conductors, Measured by the Electromagnetic Torque Produced, *Keith K. Smith*, 402.

Clark, Harry, A Test for X-Ray Refraction Made with Monochromatic Rays, 528.

Compton's Formula for the Temperature Variation of the Specific Heat of Solids, *F. Schwers*, 117, 753.

Compton, Karl T., The Mean Free Path of an Electron in a Gas and its Minimum Ionizing Potential, 386.

Application of the Electron Theory of Gaseous Dielectrics to the Calculation of Minimum Ionizing Potentials, 412.

The Nature of the Collisions of Electrons with Gas Molecules, 449.

Condensation, The Evaporation, and Reflection of Molecules and the Mechanism of Adsorption, *Irving Langmuir*, 149.

Conductors, Resistance and Reactance of Massed Rectangular, *A. Press*, 417.

Conductivity, The Electrical, of a Bunsen Flame for Small Distances between the Electrodes, *Norman Hurd Ricker*, 626.

Contact Electromotive Force, On the Influences Contributing to the Variation of, with Time, *Otto Stuhlmann, Jr.*, 294.
Contact Potential, Temperature Coefficient of, A Criticism, *Fernando Sanford*, 95.
Corona Discharge, On the Initial Condition of the, *Jakob Kunz*, 28.
Corona, Determination of the Laws Relating Ionization Pressure to the Current in the, of Constant Potentials, *Earle H. Warner*, 285.
Corona, Direct Current, from Different Surfaces and Metals, *Sylvan J. Crooker*, 344.
Crooker, Sylvan J., Direct Current Corona from Different Surfaces and Metals, 344.

D.

Davisson, C., The Dispersion of Hydrogen and Helium on Bohr's Theory, 20.
Demagnetization, On the, of Iron and Steel Rods by Strain and Impact, *Guy G. Becknell*, 504.
Dempster, A. J., The Properties of Slow Canal Rays, 651.
Diatomic, The Distribution of Angular Velocities Among Gas Molecules, *Edwin C. Kemble*, 689.
Dielectric Constant, The, of Aqueous Solutions, *Elmer A. Harrington*, 581.
Dieterich, E. O., The Effect of Temperature on the Light-Sensibility Curves of Different Types of Selenium Cells, 191.

E.

Echelette Grating, The, *A. Trowbridge*, 485.
Ehrenfest-Afanassjewa, T., On Mr. R. C. Tolman's "Principle of Similitude," 1.
Elastic Properties, Notes on the, of Phosphor-Bronze Wires, *Arnold J. Oehler*, 465.
Electrode Potentials, On the Electrostatic Measurements of, *G. Borelius*, 128.
Electron, The Mean Free Path of an, in a Gas and its Minimum Ionizing Potential, *Karl T. Compton*, 386.
Electrons, The Nature of the Collisions of, with Gas Molecules, *K. T. Compton* and *J. M. Benade*, 449.
Electron Theory, Application of the, of Gaseous Dielectrics to the Calculation of Minimum Ionizing Potentials, *Karl T. Compton*, 412.
Electromagnetic Torque, The Carbino Effect in Various Conductors, Measured by the, Produced, *Keith K. Smith*, 402.
Electromotive Force, The, Produced by the Acceleration of Metals, *Richard C. Tolman* and *T. Dale Stewart*, 97, 753.
Electrometer, Note on the Parson, *G. E. M. Jauncey* and *G. J. Buchner*, 248.
Electronic Charge, Some Properties of Mercury Droplets Important in, Measurements, *L. W. McKeehan*, 142.
Electrostatic Measurements, On the, of Electrode Potentials, *G. Borelius*, 128.
Energy, The Normal Photo-electric Effect of Lithium, Sodium and Potassium as a Function of Wave-length and Incident, *Wilmer H. Souder*, 310.
Errata, 753.
Evaporation, The, Condensation and Reflection of Molecules and the Mechanism of Adsorption, *Irving Langmuir*, 146.

F.

Flame, The Electrical Conductivity of a Bunsen, for Small Distances between the Electrodes, *Norman Hurd Ricker*, 626.
Fluorescence, The, and Absorption of Certain Pleochroic Crystals of the Uranyl Salts, *Edward L. Nichols* and *H. L. Howes*, 364.

G.

Gases, The Luminosity of the Positive Column in, at Low Pressures, *H. A. Wilson*, 278.
Gardner, Willard, The Photo-electric Current as a Function of the Angle of Emission and the Thickness of the Emitting Film, 66.
Gibson, K. S., The Effect of Temperature upon the Absorption Spectrum of a Synthetic Ruby, 38.
Gorton, W. S., Some Remarks on the Mica X-Ray Spectrometer of, *Manne Siegbahn*, 320.
Goucher, F. S., Ionization by Impact in Mercury Vapor and Other Gases. I. The Direct Measurement of the Ionizing Potentials, 561.
Grating, The Echelette, *A. Trowbridge*, 485.

H.

h, The value of, determined Photo-electrically from the Ordinary Metals, *W. H. Kadesch* and *A. E. Hennings*, 221.

Hall Effect, The, and Allied Phenomena in Rare Metals and Alloys, *Alpheus W. Smith*, 79.

Harmonics, On the Occurrence of, in the Infra-Red Absorption Spectra of Gases, *Edwin C. Kemble*, 701.

Harrington, Ertle Leslie, A Redetermination of the Absolute Value of the Coefficient of Viscosity of Air, 738.

Harrington, Elmer A., The Dielectric Constant of Aqueous Solutions, 581.

Helium, The Dispersion of Hydrogen and, on Bohr's Theory, *C. Davisson*, 20.

Hematite, The Magnetic Properties of, *T. Townsend Smith*, 721.

Hennings, A. E., The Relations of the Photo-Potentials Assumed by Different Metals when stimulated by Light of a Given Frequency, 209.

The Value of *h* determined Photo-electrically from the Ordinary Metals, 221.

Hilger Sector Photometer, On a Modification of the, for Measuring Ultra-violet Absorption and its Application in the Case of Certain Derivatives of Fluoran, *H. E. Howe*, 674.

Homogeneity, Note on the, of Physical Equations, *Richard C. Tolman*, 8.

Hot Water Pipes, The Frequent Bursting of, in Household Plumbing Systems, *F. C. Brown*, 500.

Howe, H. E., On a Modification of the Hilger Sector Photometer Method for Measuring Ultra-violet Absorption and its Application in the Case of Certain Derivatives of Fluoran, 674.

Howes, H. L., The Fluorescence and Absorption of Certain Pleochroic Crystals of the Uranyl Salts, 364.

Hull, Albert W., The Law of Absorption of X-Rays at High Frequencies, 326.

Hydrogen, The Dispersion of, and Helium, on Bohr's Theory, *C. Davisson*, 20.

I.

Incandescent Lamp, The Radiant Luminous Efficiency of the Carbon, and the Mechanical Equivalent of Light, *Herbert E. Ives* and *E. F. Kingsbury*, 254.

Index, 754.

Infra-Red Absorption Spectra, On the Occurrence of Harmonics in the, of Gases, *Edwin C. Kemble*, 701.

Ionization of Gases, On the, by Alpha Rays, *H. A. Bumstead*, 715.

Ionization by Impact in Mercury Vapor and Other Gases. I. The Direct Measurement of the Ionizing Potentials, *F. S. Goucher*, 561.

Ionizing Potential, The Mean Free Path of an Electron in a Gas and its Minimum, *Karl T. Compton*, 386.

Ionizing Potentials, Application of the Electron Theory of Gaseous Dielectrics to the Calculation of Minimum, 412.

Ionizing Potentials, The Direct Measurement of the, Ionization by Impact in Mercury Vapor and Other Gases, *I. E. S. Goucher*, 561.

Ions, On the Mobilities of Gas, in High Electric Fields, *Leonard B. Loeb*, 633.

Ionization Pressure, Determination of the Laws Relating, to the Current in the Corona of Constant Potentials, *Earle H. Warner*, 285.

Iron Oxide, Resistance and Thermo-electric Relations in, *C. C. Bidwell*, 12.

Ives, Herbert E., The Mechanical Equivalent of Light as Determined from the Brightness of the Black Body, 177.

The Black Body at the Melting Point of Platinum as a Fixed Point in Photometry, 250.

The Radiant Luminous Efficiency of the Carbon Incandescent Lamp at the Mechanical Equivalent of Light, 254.

Note on Black Body Brightness Equation Based on Equivalent Wave-Lengths, 323.

J.

Jauncey, G. E. M., Note on the Parson Electrometer, 248.

Jensen, J. C., A Comparison of Alternating and Direct Spark Potentials, 433.

Jones, Lloyd T., An Experimental Verification of the Law of Variation of Mass with Velocity for Cathode Rays, 52.

K.

Kadesch, W. H., The Relations of the Photo-Potentials Assumed by Different

Metals when Stimulated by Light of a Given Frequency, 209.

The Value of h determined Photo-electrically from the Ordinary Metals, 221.

Kemble, Edwin C., The Distribution of Angular Velocities Among Diatomic Gas Molecules, 689.

On the Occurrence of Harmonics in the Infra-Red Absorption Spectra of Gases, 701.

Kingsbury, E. F., The Mechanical Equivalent of Light as Determined from the Brightness of the Black Body, 177.

The Radiant Luminous Efficiency of the Carbon Incandescent Lamp and the Mechanical Equivalent of Light, 254.

Note on Black Body Brightness Equation Based on Equivalent Wave-Lengths, 323.

Klopsteg, Paul E., The Measurement of Time with a Moving Coil Galvanometer, 195.

Kovarik, Alois F., The Magnetic Spectra of the β-Rays of Radium De and of Radium and its Products, Determined by the Statistical Method, 574.

Kunz, Jakob, On the Initial Condition of the Corona Discharge, 28.

L.

Langmuir, Irving, A High Vacuum Mercury Vapor Pump of Extreme Speed, 48.

The Evaporation, Condensation and Reflection of Molecules and the Mechanism of Adsorption, 149.

Light, The Mechanical Equivalent of, as Determined from the Brightness of the Black Body. *Herbert E. Ives* and *E. F. Kingsbury*, 177.

Light, The Reflection Coefficients of Metals for the Polarized Components of, *R. B. Wilsey*, 391.

Light-Sensibility, The Effect of Temperature on the, Curves of Different Types of Selenium Cells, *E. O. Dieterich*, 191.

Lithium, The Normal Photo-electric Effect of, Sodium, and Potassium as a Function of Wave-Length and Incident Energy, *Wilmer H. Souder*, 310.

Loeb, Leonard B., On the Mobilities of Gas Ions in High Electric Fields, 633.

Luminosity, The Luminosity, of the Positive Column in Gases at Low Pressures, *H. A. Wilson*, 278.

M.

McDowell, Louise S., A Study of the Law of Response of the Silicon Detector, 133.

McKeehan, L. W., Some Properties of Mercury Droplets Important in Electronic Charge Measurements, 142.

The Magnetic Spectra of the β-Rays of Radium De and of Radium and its Products, Determined by the Statistical Method, 574.

Markwell, Effie, The Coefficient of Viscosity of Air by the Capillary Tube Method, 479.

Mechanical Equivalent, The, of Light as Determined from the Brightness of the Black Body, *Herbert E. Ives* and *E. F. Kingsbury*, 177.

Mechanical Equivalent, The Radiant Luminous Efficiency of the Carbon Incandescent Lamp and the, of Light, *Herbert E. Ives* and *E. F. Kingsbury*, 254.

Mercury Vapor Pump, A High Vacuum of Extreme Speed, *Irving Langmuir*, 48.

Moving Coil Galvanometer, The Measurement of Time with a, *Paul E. Klopsteg*, 195.

Mercury Droplets, Some Properties of, Important in Electronic Charge Measurements, *L. W. McKeehan*, 142.

Millikan, R. A., The Existence of a Sub-electron?, 595.

Moffitt, G. W., A Direct Reading Precision Refractometer with Uniformly Divided Scale, 663.

Molecules, The Nature of the Collisions of Electrons with Gas, *K. T. Compton* and *J. M. Benade*, 449.

Molybdenum, Thermionic Currents from, *E. R. Stoekle*, 534.

Miller, C. D., The Absorption Coefficients of Soft X-Rays, 329.

N.

New Books, 432, 579, 752.

Nichols, Edward L., The Fluorescence and Absorption of Certain Pleochroic Crystals of the Uranyl Salts, 364.

O.

Oehler, Arnold J., Notes on the Elastic Properties of Phosphor-Bronze Wires, 465.

P.

Page's Theory of Heat Radiation, Notes on, *David L. Webster*, 66.

Phosphor-Bronze Wires, Notes on the Elastic Properties of, *Arnold J. Oehler*, 465.

Photo-electric Current, The, as a Function of the Angle of Emission and the Thickness of the Emitting Film, *Willard Gardner*, 66.

Photo-electric Effect, The Influence of Occluded Gases on the, *Robert James Piersol*, 238.

Photo-electric Effect, The Normal, of Lithium, Sodium and Potassium as a Function of Wave-Length and Incident Energy, *Wilmer H. Souder*, 310.

Photo-Potentials, The Relations of the, Assumed by Different Metals when Stimulated by Light of a Given Frequency, *A. E. Hennings* and *W. H. Kadesch*, 209.

Photometer Method, On a Modification of the Hilger Sector, for Measuring Ultra-violet Absorption and its Application in the Case of Certain Derivatives of Fluoran, *H. E. Howe*, 674.

Photometry, The Black Body at the Melting Point of Platinum as a Fixed Point in, *Herbert E. Ives*, 250.

Physical Equations, Note on the Homogeneity of, *Richard C. Tolman*, 8.

Piersol, Robert James, The Influence of Occluded Gases on the Photo-electric Effect, 238.

Platinum, The Black Body at the Melting Point of, as a Fixed Point in Phtoometry, *Herbert E. Ives*, 250.

Pleochroic Crystals, The Fluorescence and Absorption of certain, of the Uranyl Salts, *Edward L. Nichols* and *H. L. Howes*, 364.

Potassium, The Normal Photo-electric Effect of Lithium, Sodium, as a Function of Wave-Length and Incident Energy, *Wilmer H. Souder*, 310.

Press, A., Resistance and Reactance of Massed Rectangular Conductors, 417.

R.

Radiation, Notes on Page's Theory of Heat, *David L. Webster*, 66.

Radium De, The Magnetic Spectra of the β-Rays of, and of Radium and its Products, Determined by the Statistical Method, *Alois F. Kovarik* and *L. W. McKeehan*, 574.

Reactance, Resistance and, of Massed Rectangular Conductors, *A. Press*, 417.

Reflection, The Evaporation, Condensation and, of Molecules and the Mechanism of Adsorption, *Irving Langmuir*, 149.

Reflection Coefficients, The, of Metals for the Polarized Components of Light, *R. B. Wilsey*, 391.

Refractometer, A Direct Reading Precision, with Uniformly Divided Scale, *G. W. Moffitt*, 63.

Resistance and Thermo-electric Relations in Iron Oxide, *C. C. Bidwell*, 12.

Resistance, Change of, with Temperature of Various Sodium Amalgams, *Ralph C. Rodgers*, 259.

Resistance and Reactance of Massed Rectangular Conductors, *A. Press*, 417.

Rice, Marion, The Law of Absorption of X-Rays at High Frequencies, 326.

Ricker, Norman Hurd, The Electrical Conductivity of a Bunsen Flame for Small Distances between the Electrodes, 626.

Rodgers, Ralph C., Change of Resistance with Temperature of Various Sodium Amalgams, 259.

Ruby, The Effect of Temperature upon the Absorption Spectrum of a Synthetic, *K. S. Gibson*, 38.

S.

Sanford, Fernando, The Specific Inductive Capacity of Certain Metals, 89.

Temperature Coefficient of Contact Potential, A Criticism, 95.

Schwers, F., Compton's Formula for the Temperature Variation of the Specific Heat of Solids, 117, 753.

Seigbahn, Manne, Some Remarks on the Mica X-Ray Spectrometer of, *W. S. Gorton*, 320.

Selenium Cells, The Effect of Temperature on the Light-Sensibility Curves of Different Types of, *E. O. Dieterich*, 191.

Shackelford, B. E., Temperature and Blackening Effects in Helical Tungsten Filaments, 470.

Silicon Detector, A Study of the Law of Response of the, *Louise S. McDowell* and *Frances G. Wick*, 133.

Similitude, On Mr. R. C. Tolman's Principle of, *T. Ehrenfest-Afanassjewa*, 1.

Similitude, Tolman's Principle of, *P. W. Bridgman*, 423.

Smith, Alpheus W. The Hall Effect and allied Phenomena in Rare Metals, and Alloys, 79.

Smith, Keith K., The Carbino Effect in Various Conductors, Measured by the Electromagnetic Torque Produced, 402.

Smith, T. Townsend, The Magnetic Properties of Hematite, 721.

Sodium, The Normal Photo-electric Effect of Lithium, and Potassium as a Function of Wave-Length and Incident Energy, *Wilmer H. Souder*, 310.

Souder, Wilmer H., The Normal Photo-electric Effect of Lithium, Sodium and Potassium as a Function of Wave-Length and Incident Energy, 294.

Spark Potentials, A Comparison of Alternating and Direct, *J. C. Jensen*, 433.

Specific Heat, Compton's Formula for the Temperature of the, of Solids, *F. Schwers*, 117.

Specific Inductive Capacity of Certain Metals, *Fernando Sanford*, 89.

Stewart, T. Dale, The Electromotive Force Produced by the Acceleration of Metals, *Richard C. Tolman* and *T. Dale Stewart*, 97, 753.

Stoekle, E. R., Thermionic Currents from Molybdenum, 534.

Stuhlmann, Jr., Otto, On the Influences Contributing to the Variation of Contact Electromotive Force with Time, 294.

Subelectron, The Existence of a, *R. A. Millikan*, 595.

T.

Taylor, E. G., Phenomena Attending the Passage of X-Rays through Narrow Apertures, 207.

Temperature Coefficient of Contact Potential, A Criticism, *Fernando Sanford*, 95.

Thermo-electric Relations, Resistance and, in Iron Oxide, *C. C. Bidwell*, 12.

Thermionic Currents from Molybdenum, *E. R. Stoekle*, 534.

Time, The Measurement of, with a Moving Coil Galvanometer, *Paul E. Klopsteg*, 195.

Tolman's Principle of Similitude, *T. Ehrenfest-Afanassjewa*, 1.

Tolman, Richard C., Note on the Homogeneity of Physical Equations, 8.

The Electromotive Force Produced by the Acceleration of Metals, 97, 753.

Tolman's Principle of Similitude, *P. W. Bridgman*, 423.

Trowbridge, A., The Echelette Grating, 485.

Tungsten Filaments, Temperature and Blackening Effects in Helical, *B. E. Shackelford*, 470.

U.

Uranyl Salts, The Fluorescence and Absorption of Certain Pleochroic Crystals of the, *Edward L. Nichols* and *H. L. Howes*, 364.

V.

Variation of Mass, An Experimental Verification of the Law, with Velocity for Cathode Rays, *Lloyd T. Jones*, 52.

Viscosity, The Coefficient of, of Air by the Capillary Tube Method, 479.

Viscosity, A Redetermination of the Absolute Value of the Coefficient of, of Air, *Ertle Leslie Harrington*, 238.

W.

Warner, Earle H., Determination of the Laws Relating Ionization Pressure to the Current in the Corona of Constant Potentials, 285.

Wave-Length, The Normal Photo-electric Effect of Lithium, Sodium, Potassium, as a Function of, and Incident Energy, *Wilmer H. Souder*, 310.

Webster, David L., Notes on Page's Theory of Heat Radiation, 66.

A Test for X-Ray Refraction Made with Monochromatic Rays, 528.

Wick, Frances G., A Study of the Law of Response of the Silicon Detector, 133.

Wilsey, R. B., The Reflection Coefficients of Metals for the Polarized Components of Light, 391.

Wilson, H. A., The Theory of the Cathode Fall of Potential, 227.

Wilson, H. A., The Luminosity of the Positive Column in Gases at Low Pressures, 278.

X.

X-Rays, The Absorption Coefficients of Soft, *C. D. Miller*, 329.

X-Rays, The Law of Absorption of, at High Frequencies, *Albert W. Hull* and *Marion Rice*, 326.

X-Rays, Phenomena Attending the Passage of, through Narrow Apertures, *E. G. Taylor*, 207.

X-Ray Refraction, A Test for, Made with Monochromatic Rays, *Harry Clark*, 528.

X-Ray Spectrometer, Some Remarks on the Mica, of W. S. Gorton, *Manne Seigbahn*, 320.

THE TYPE R GALVANOMETER

This instrument is the latest addition to our galvanometer line. It is patterned after our No. 2285 High Sensitivity Galvanometer and includes many of the desirable features of that instrument. The sensitivity of the type R instrument is higher than that of any galvanometer we have ever offered except the No. 2285 instrument mentioned above.

NOTE THE FOLLOWING BRIEF SPECIFICATIONS:

Magnet—Of special steel, with pole pieces so shaped as to produce a radial field. **Coil**—Wound of carefully selected wire, as free as possible from magnetic impurities. **Suspensions**—Of silver strip rolled in our own factory. **Mirror**—½" in diameter. **Adjustment**—Under the small cap shown on the top of the case of the galvanometer is a knurled head by means of which the coil may be turned for zero adjustment. **Arrestment**—Convenient means are provided for lifting the coil to protect the suspension. **Detail**—The galvanometer is enclosed in a cylindrical metal case, finished in black, with a large glass window in front. The instrument is mounted upon an insulating base supported upon three leveling screws. **Setting Up**—The air gaps are large in comparison to the size of the coil so that the instrument is very easily set up. To facilitate setting up a level is mounted upon the base of the instrument. **Removable System**—The entire system is easily removable to facilitate the replacing of the suspensions.

SENSITIVITY SPECIFICATIONS

Type	Resistance Ohms	Sensitivities	Period Seconds	Critical Damping Resistance External
a	10	2 mm. per microvolt *	6	50
b	550	{ 2000 megohms { 5×10^{-10} amperes	6	11,500

***Including critical damping resistance in series.**

Descriptive literature will be sent upon request

THE LEEDS & NORTHRUP CO.

ELECTRICAL MEASURING INSTRUMENTS

4900 STENTON AVENUE PHILADELPHIA

THE PHYSICAL REVIEW

Information for Contributors.

1. All correspondence relating to contributions should be addressed to THE PHYSICAL REVIEW, Ithaca, N. Y. Manuscripts will be acknowledged as soon as received. Articles submitted for publication in the REVIEW are not to be submitted for publication elsewhere unless the authorization of the editors has been obtained, and, in case of duplicate publication in English, proper reference to the REVIEW is made. Manuscript should be ready for the printer; the editors cannot assume responsibility for its correctness. The presentation should be as concise as is consistent with clearness; all unnecessary duplication of data in tables and in curves is to be avoided, and tabular matter should be introduced *in extenso* only when the exact numerical values affect the value of the paper. It is requested that the metric system be used in all cases. Whenever the value of a quantity is expressed in any other system, its value in the metric system should be added in parentheses.

To insure prompt attention during the summer, manuscripts should be submitted by June 15.

2. Illustrations should be in black and white and should be ready for direct reproduction; such illustrations will be made without expense to the author. The ink used in preparing illustrations should be *jet black*. Curves can be satisfactorily reproduced when plotted on plain paper or on blue-lined cross-section paper; co-ordinates may be ruled in black at desired intervals, for example every centimeter or every inch. Blue lines are not reproduced photographically; *colors other than jet-black and blue should be avoided*. The material in an illustration should be compactly arranged; when it is much spread out, a greater reduction is necessary in reproduction. Lettering on illustrations should be plain and of sufficient size to be legible after reduction.

It is generally desirable to refer to *all* illustrations as "figures," designated by one consecutive series of numbers. The location of each figure should be marked in the manuscript, together with any caption which is to be printed beneath it.

3. A proof of each contributed article will be sent to the author for his approval. It is requested that all proof be returned promptly. Authors should note that cross reference can not well be made by page number, for a change in paging is often necessary in the final make-up.

Although proof of abstracts can usually be submitted to authors, this is not always possible without delay in publication; in the case of abstracts, therefore, it is particularly important that the manuscript be free from error. In revising proof of abstracts, authors should correct any errors of the printer, but should make no changes that will affect the arrangement of paging.

4. Offprints, ordered on the proper form with return of proof, will be furnished by the printer according to the prices given below. Any special instructions in regard to offprints,—special title page, etc.,—should be indicated on the order to the printer (or attached thereto) and not as a letter to the editors. (Further inquiries in regard to offprints may be addressed to The New Era Printing Co., Lancaster, Pa.)

CHARGE FOR OFFPRINTS

Copies	4 pp.	8 pp.	12 pp.	16 pp.	20 pp.	24 pp.	28 pp.	32 pp.	48 pp.	64 pp.
50	$1.45	$1.95	$2.60	$2.92	$3.67	$4.30	$5.20	$5.70	$8.10	$10.60
75	1.60	2.30	3.05	3.45	4.70	4.95	6.10	6.60	9.45	11.05
100	1.80	2.60	3.50	3.95	5.10	5.90	7.00	7.50	10.85	13.05
150	2.05	3.05	4.20	4.85	6.75	6.95	7.35	9.15	13.20	17.55
200	2.35	3.75	5.25	6.15	7.85	8.75	10.45	11.05	16.35	21.65
300	2.95	4.75	5.85	8.15	10.60	11.90	1 .10	14.85	22.15	29.55

Covers: 50 covers for $1.00, and 1c. for each additional cover.

Prices subject to change on account of changing cost of paper.

Scientific Apparatus of Special Nature

Optical Pyrometers—Polariscopes—High Vacuum Pumps—High Pressure Gas Compressors (200 atm.)—Gas Refractometers—Metallographic Equipment — Hardness Testers — Zeiss Microscopes — Luminescence Microscopes—Platinum Substitutes.

If in the market for any kind of special apparatus not easily obtainable at this time, please write to me. I can help you and save you money.

HERMAN A. HOLZ

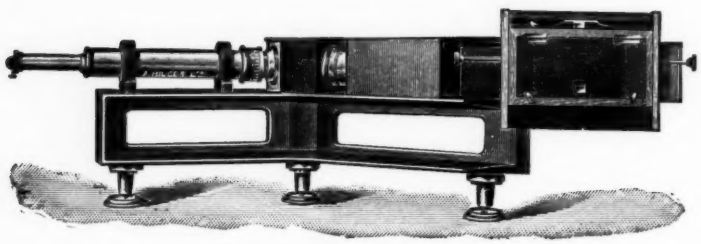
50 Church Street NEW YORK

Specialist in Scientific Instruments of High Quality

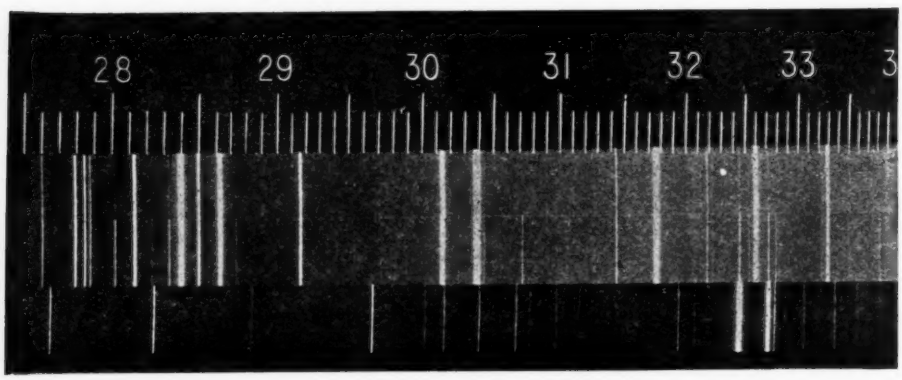
HILGER QUARTZ SPECTROGRAPH

Size C.

WITH WAVELENGTH SCALE



The following print is a process reproduction, enlarged three times, of a portion of three comparison spectra taken on one of these Spectrographs adapted with Wavelength Scale.



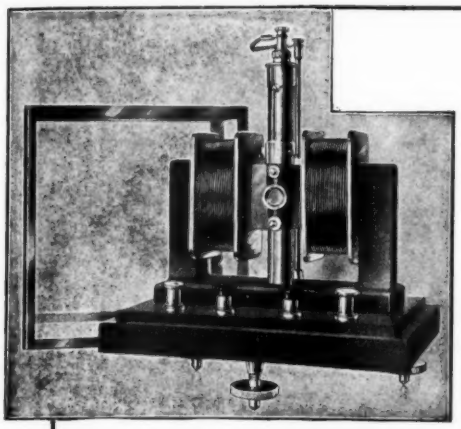
We can now supply apparatus for Spectrophotometry in the Ultra-Violet designed for use with these Spectrographs.

Full particulars post free on application to

ADAM HILGER Ltd.

75 A. Camden Road **LONDON, N. W.**

Telegraphic address "Sphericity, London." Cable Code---Western Union. (4)



P. J. KIPP & ZONEN
DELFT-Holland

Rapid Coil-Galvanometer

Constructed by Dr. Moll
Aperiodical indication within 1.5 sec.
Sensitiveness: 5 mm. on a scale at 1 Meter distance for 1 microvolt.

Rapid Thermopiles

Constructed by Dr. Moll
Equilibrium of temperature within 2 sec.
Sensitiveness: 100 microvolt for one candle at 1 Meter distance.

SELENIUM CELLS OF HIGH SENSITIVENESS

MICROTOMES for sections from 1 to 80 micron.

Lists and full information by the importers:

Mr. JAMES G. BIDDLE, 1211-13 Arch Street, Philadelphia.

Messrs. WOLDENBERG & SCHAAR, 1025 South State Street, Chicago.

THE BRAUN CORPORATION, 363-71 New High Street, Los Angeles, Cal. (A)

W. G. PYE & CO., Granta Works, Cambridge, England

GALVANOMETERS
POINTER TYPE

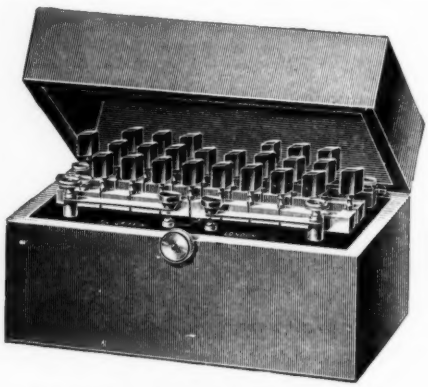
In the design of these instruments we have given careful attention to strength of suspension, ease of repairing and ease of levelling. The system is a light moving coil, "spring" suspended on phosphor bronze. An automatic lifting arrangement clamps the coil when the instrument is lifted, and a safety stop is provided to prevent overtwisting the suspension. The case is of a tough aluminium alloy.

Price - - - - $12.00 I

Discount upon Application

JOHN J. GRIFFIN & SONS LTD

KEMBLE ST. KINGSWAY LONDON, W. C.

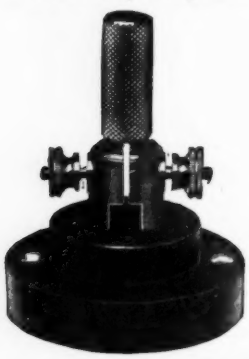


Set of Resistance Coils and Wheatstone Bridge, P. O. pattern; three coils in proportional arms; 1 to 5000 in third arm. £7.40

Makers of Physical and Electrical Apparatus to the British War Office, Admiralty, India Office and Colonial Governments

Gambrells' Patent "Independent" Plug Contact

For Resistance Boxes, Wheatstone Bridges, Switches, etc., etc.



In use by H. M. Government, Leading Telegraph Companies, Cable Manufacturers, Electricity Works, etc., etc.

The only Resistance Box contact with plugs entirely independent of each other. One standard size, all plug caps interchangeable, independent of type of instrument. Large surface contact. No plug heads to give trouble. High insulation, each unit self assembling. Can be more quickly used.

GAMBRELL BROS., Ltd.

Makers of Galvanometers, Resistance Boxes, Potentiometers, etc.

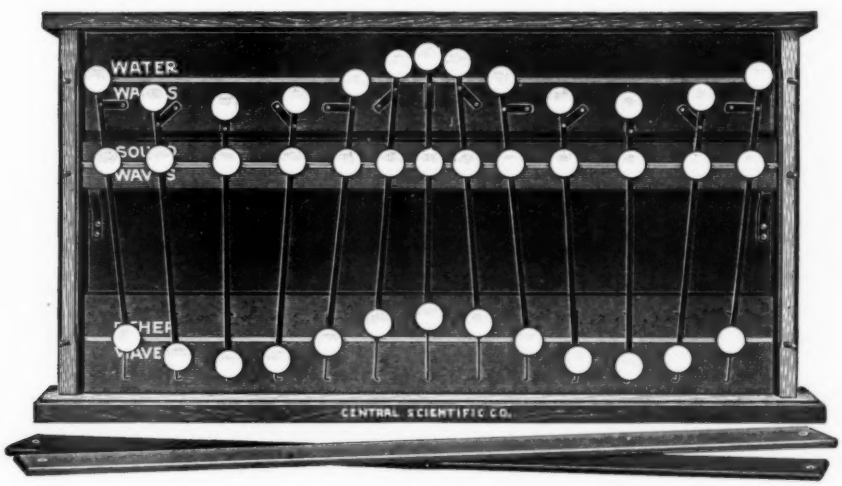
Head Office and Works, MERTON ROAD, SOUTHFIELDS, LONDON, ENGLAND

HAVE YOU THE BEST CROSS SECTION PAPER

In view of the quantity of cross section paper which we are selling, we are confident that we are supplying a good article at a reasonable price. If you are using cross section paper, it would certainly be worth your while to have our sample book in your file. The sample book shows the quality of paper used and the colors of ink. We will print special for you in lots of five hundred sheets or over.

Cornell Co-operative Society

Morrill Hall **Ithaca, New York**



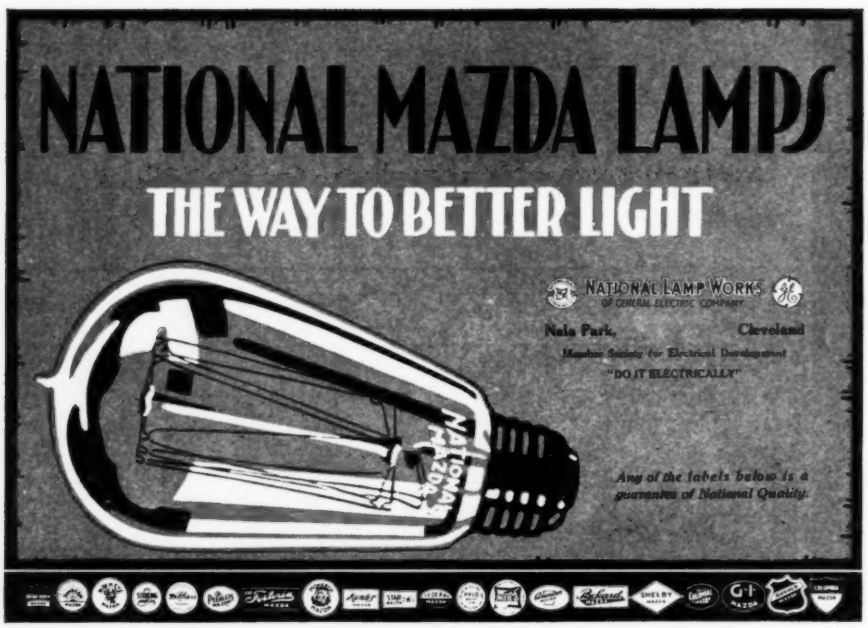
No. 3174

COLUMBIA WAVE MACHINE

The Invention of Dr. Charles Forbes of Columbia University. Demonstrates Water Waves; Sound Waves; Ether Waves. Send for Complete Description

CENTRAL SCIENTIFIC COMPANY

460 East Ohio Street **CHICAGO, U. S. A.**


NATIONAL MAZDA LAMPS
THE WAY TO BETTER LIGHT
NATIONAL LAMP WORKS
OF GENERAL ELECTRIC COMPANY
Nela Park,
Cleveland
"DO IT ELECTRICALLY"
Any of the labels below is a guarantee of National Quality.

MORSE TWIST DRILL & MACHINE COMPANY New Bedford, Mass.

Makers of Twist Drills, Reamers, Cutters, Etc.

TOOLS THAT PROVE THEIR WORTH.

Laboratory Spectrometers

SPECIALTIES

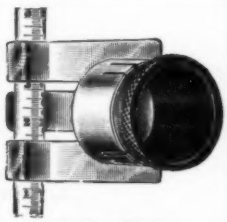
High Grade Measuring Instruments to cover all requirements

Laboratory and demonstration apparatus for advanced and elementary work

Full line Calorimeters

Universal Laboratory Supports

General Laboratory Supplies



Reading Device for Thermometers $1.80

WM. GAERTNER & CO., 5345-49 Lake Park Ave., Chicago

The Langmuir Condensation Pump

Dr. Irving Langmuir (of the General Electric Company) has developed an exceedingly interesting and valuable *high-speed, high-vacuum pump;* and by special arrangement with the makers, we are acting as sole distributors of this device, for laboratory purposes.

As shown in accompanying illustration, the pump is manufactured entirely of metal; and thus is far more permanent in character than would be possible if glass were used.

Connections are provided for water cooling; and beneath the pump is a small electric heater (terminals not shown in picture) for attachment to 110 volt lighting circuit.

With the Langmuir Pump pressures as low as 10^{-5} bar have been obtained, and there is little doubt that very much lower pressures can be produced by cooling the bulb to be exhausted, in liquid air, so as to decrease the rate at which gases escape from the walls.

As is known to physicists, one "bar" is equal to 0.00075 mm. of mercury.

Some type of primary pump must be used; capable of developing a vacuum not less than 0.1–0.15 mm of mercury.

In the December 1916 issue of General Electric Review, Dr. Langmuir will publish a paper entitled—"The Condensation Pump, an Improved Form of High-Vacuum Pump." It should be read by all scientists who are interested in high-vacuum work.

$90.00 is the net price for a Langmuir Condensation Pump

JAMES G. BIDDLE, PHILADELPHIA

1211-13 Arch St.

Be sure to visit our Permanent Exhibit of Scientific Instruments

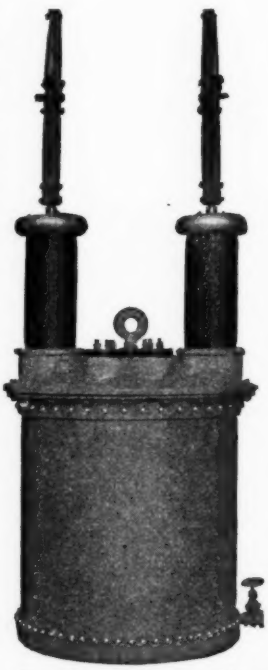
300,000 Volt Testing Transformer.

High Voltage Testing Equipment

The engineers of the General Electric Company have an intimate knowledge of the severe conditions under which testing transformers must operate. This knowledge has been acquired in the extensive high voltage research work of this Company, and in the commercial testing of large quantities of raw materials and of completed high voltage apparatus. This exact knowledge has been applied to the design of a standardized line of testing transformers known as Type "K." This line will meet every requirement.

In all Type "K" designs, circular coil construction is used, and careful attention has been given to the mechanical as well as to the electrical stresses that must be withstood.

If you need testing equipment, the recommendations of our engineers are at your service.



Transformer for use with Cottrell Precipitation Process.

General Electric Company

General Office: Schenectady, N. Y.

District Offices in

Boston, Mass. New York, N. Y. Philadelphia, Pa. Atlanta, Ga. Cincinnati, Ohio
Chicago, Ill. Denver, Colo. San Francisco, Cal. St. Louis, Mo. 6457

WANTED

Young man with at least two years of graduate work in Physics, and with good training in Optics and knowledge of Chemistry, for position in newly established research laboratory. State qualifications, experience, etc., in first letter. Address replies to Box R, care of Physical Review.

WANTED

Physicist of the Electrical Discharge line for Research and Development work in new Engineering Work for a manufacturing company in Middle West. Good prospects for man with initiative. State full particulars in first letter. Box No. X, care Physical Review.

WANTED

Laboratory mechanic and glass blower with experience in electrode work for factory in Middle West. Give full details with wages expected in first letter. Box No. Y, care Physical Review.

WANTED

Glass Blower having experience in electrode work. Give full particulars and wages expected. Box No. Z, care Physical Review.

Weston

Alternating Current Switchboard Instruments

AMMETER

VOLTMETER

WATTMETER
Single and Polyphase

possess to a marked degree those qualities of originality and excellence of mechanical and electrical design and construction that distinguish WESTON products from all others, and we claim for them a perfection with respect to accuracy, reliability, serviceability and durability that is unapproached.

These Instruments are the perfected product of many years of specialization. The modern art of commercial electrical measurement was created by the founder of this Company. Our immense plant is devoted exclusively to the manufacture of the world's highest-grade Electrical Instruments of precision.

Write for Catalog 16

Weston Electrical Instrument Co.

25 Weston Avenue, Newark, N. J.

New York	Chicago	Detroit
Boston	St. Louis	San Francisco
Philadelphia	Pittsburgh	Toronto
Buffalo	Richmond	Montreal
Cleveland	Denver	Winnipeg
Cincinnati		Vancouver